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The Thermal Precipitation of Hydrated Titanium Oxide from Titanium Sulphate Solutions

DISSERTATION

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By

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ABSTRACT.

Foreword:

Titanium is used extensively in pigments for paint, lacquer, enamel, rubber, etc. In the preparation of titanium pigments, whether of pure titanium oxide or composites of titanium oxide and extenders such as barium sulphate or calcium sulphate, nearly all processes involve the hydrolysis of a titanium sulphate solution to precipitate, either alone or on an extender, a hydrated titanium oxide which is dried and calcined to form the pigment.

Purpose of the investigation:

A survey of the literature showed that there exists no quantitative data on the hydrolysis of titanium sulphate solutions other than that concerned with its hydrolytic separation in quantitative analysis wherein excessively dilute solutions are used. It was thought therefore that since the hydrolysis of titanium sulphate solutions is of great importance in the industry, that a quantitative study of some of the factors effecting the precipitation reactions would prove of interest and importance. This investigation was carried out with solutions covering the range of titanium oxide concentrations and of acidities used in the industry in order to determine the influence of titanium concentration and acidity on the course of precipitation.

Method of attack:

Pure solutions of titanium sulphate were prepared by hydrolyzing re-distilled titanium tetrachloride in the presence of titanous chloride and oxalic acid, dissolving the hydrated titanium oxide so obtained in sulphuric acid and crystallizing titanyl sulphate dihydrate which was dissolved in water acidified with sulphuric acid to form the desired solutions. These solutions of titanium sulphate, varying in concentration from one to ten per cent of titanium oxide by weight and of selected acid concentration, were hydrolyzed by boiling under a reflux condenser, or in some cases heating in sealed jars at 100° C., and the progress of the hydrolysis observed analytically.

Results and conclusions:

1. A method of preparing pure titanium sulphate solutions was devised.

2. Precipitation, in the titanium sulphate solutions studied, does not increase regularly with dilution.

3. With increasing concentration, precipitation in a given time period decreases to a minimum value; with further increase in concentration precipitation increases to a maximum; and then decreases again.

4. The maximum and minimum points in the precipitation occur at specific concentrations of titanium oxide at each acidity used.

5. In the industrial precipitation of titanium oxide by hydrolysis it is necessary to regulate the acidity as well as the titanium oxide concentration in order to economically obtain high yields.

6. With increased acidity the titanium oxide concentration of the titanium sulphate solutions in which maximum precipitation occurs is lower.

7. The maximum per cent precipitated in the time periods studied decreases with increased acidity.

8. Titanium sulphate solutions may be more than 95 per cent precipitated by boiling for less than eight hours when such contain six to ten per cent of titanium oxide, and the ratio of excess sulphuric acid to titanium oxide is one or less than one.

9. Titanyl sulphate dihydrate is crystallized by heating solutions of titanium sulphate in which the titanium oxide concentration is more than six per cent and the ratio of excess sulphuric acid to titanium oxide is two or more. It is possible in this way to prepare relatively pure water-soluble crystalline titanyl sulphate on an industrial scale.

The Thermal Precipitation of Hydrated Titanium Oxide from Titanium Sulphate Solutions

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INTRODUCTION.

Titanium which ranks as one of the more abundant elements, is widely distributed, and occurs in concentrated ore deposits of commercial importance in Virginia and Florida in the United States, Quebec Province in Canada, Brazil, Norway, the east coast of Africa, Madagascar, Travancore in India, and elsewhere. Although discovered toward the end of the eighteenth century it is only within the last ten or fifteen years that the use of titanium has become of industrial significance. Indicative of the increasing importance of titanium is the fact that the United States Department of Commerce has published a review which summarizes the titanium industry, with special reference to its economic aspects.[1]

Ferroalloys containing the element were largely used for a time, especially in connection with the manufacture of Bessemer steel rails; but as American railways adopted open-hearth rails in preference to Bessemer rails, the demand for the alloys in rail manufacture gradually dwindled into insignificance. New outlets for ferrotitanium have been found in the steel industry; and the production of titanium alloys, both in the United States and in Europe, has increased in recent years. It is also finding use as an alloy in welding rods. H. Rohrig claims optimum mechanical properties and resistance to organic acids is obtained in aluminum containing 0.5-1 per cent titanium.[2] Other lesser but also important uses include titanium salts as reducing or stripping agents and as mordants in the dyeing industry (textiles and leather), as a refractory pigment in the ceramic industry, and as incandescent media. Miscellaneous minor uses are the following:[3] certain titanous salts as acid-reducing agents; titanous sulphate in decolorizing old paper and dyed fabrics and in detecting copper in dyed goods and fluorine in analytical work; titanous chloride in removing iron stains in laundries and in cleaning goods that have run in the washing; titanium dioxide in the manufacture of cata-

lysts used in the esterification of acetic acid; logwood-titanium compound in making a permanent ink, deep-black in color, which undergoes no change after using; certain salts, especially the sulphates and salicylates, in therapeutics; titanium nitride as a basis for fertilizers; and titanium tetrachloride in forming smoke screens.

By far the largest use of titanium at the present time, however, is in pigments for paints, lacquers, enamels, rubber, paper, cosmetics, and soaps.

The first use of titanium compounds as pigments was about 1870 by Dr. J. Overton who mixed rutile with a bituminous vehicle for use as a resistant paint on ships' bottoms, and by J. W. Rylands, a Birmingham varnish maker, who used powdered ilmenite ore as a black pigment. In 1893 Kidwell obtained a patent covering a paint containing rutile.[4] In 1908 the Norwegian government made researches for the purpose of extracting titanium from titanium ore and finding a use for it. Titanium oxide was extracted (by means of sulphuric acid) and found to have high hiding power. Further research into titanium white as a pigment was stimulated at about this time by legislation in Europe against the use of white lead. However, it was not until 1915 that L. E. Barton secured his patent covering the first chemically prepared substantially iron free titanium pigment.[5] In 1916 two companies, Titanium Pigment Company, Inc., of the United States and Titan Company, A./S. of Norway, were organized for the manufacture of titanium pigments. In 1928 the second company producing titanium pigments in the United States, Commercial Pigments Company, began operations. The National Lead Company acquired control of the Titanium Pigment Company in 1917, and of the Titan Company and the Societe Industrielle du Titane of France in 1927. The I. G. Farbenindustrie also entered the combine. In 1931 the Commercial Pigments Company merged into the Krebs Color and Pigment Company controlled by E. I. du Pont de Nemours Corporation and Commercial Solvents Corporation. The Vanadium Corporation of America began operations at Piney River, Va., in April, 1931, for the production of titanium pigments. In Canada, Titanium, Ltd., is expected to begin operations shortly. In Europe, besides the Titan Company, the largest producer, other firms are the Deutsche Gasgluhlicht Auer Gesellschaft (Germany), the Aussig interests in Czecho-

slovakia, the Societa Anonima di Titanium, a subsidiary of the Montecatini Company of Italy, and the Fabrique de Thann et de Mulhouse, France.

In the preparation of titanium pigments, whether of pure titanium oxide or a composite, all processes involve the hydrolysis of a titanium solution to precipitate either alone or on an extender a hydrated oxide which is dried and calcined to form the pigment.[6]

In spite of the long period of time, some 140 years, that titanium has been known, and its present increasing importance, there exists no quantitative data on the hydrolysis of titanic sulphate solutions other than that concerned with its hydrolytic separation in quantitative analysis. It was thought, therefore, that since the hydrolysis of titanium sulphate solutions is of great importance in the industry, that a quantitative study of some of the conditions affecting the precipitation reactions would prove of interest and importance. This investigation was carried out with solutions covering the range of titanium oxide concentrations and of acidities commonly used in the industry. The results of the work are presented below.

HISTORICAL.

From the voluminous literature on titanium chemistry the following references, of some 3500 examined, have been selected as being pertinent to this problem.

Titanic acid may be precipitated by ammonium hydroxide from a cold solution of a titanium salt as orthotitanic acid, $Ti(OH)_4$, in which case it forms a voluminous white precipitate, which is readily soluble in dilute acid; though even this passes partially into the insoluble form if kept in contact with water for a sufficient length of time.[7] On the other hand metatitanic acid, H_2TiO_3, is precipitated from hot solution. Thus boiling of a dilute aqueous solution is attended by the precipitation of the meta-acid. The first clear recognition of these two distinct forms of titanic hydrate was not made until 1844,[8] although the hydrolysis of titanium solutions by boiling, to precipitate a titanic acid was known prior to this.[9] The precipitation occurs more readily in the presence of a sulphate or sulphuric acid, owing to the inferior stability of titanium sulphate.[10] The meta-acid is a white

powder, insoluble in water, almost insoluble in dilute acids, and soluble in hot concentrated sulphuric acid. The meta-acid when heated suffers gradual loss of water and is completely dehydrated at 710° C. without the formation of definite hydrates.[11] The titanic acids are completely amorphous as shown by X-ray examination.[12]

While there are numerous references in the literature to the hydrolysis of titanium solutions for the precipitation of metatitanic acid, in only few cases were pure solutions of titanium sulphate used, and in all cases the solutions were far too dilute to be of any industrial interest. Even concerning dilute and impure solutions no quantitative data on the conditions under which practically complete precipitation of titanium as metatitanic acid from mineral acid solutions is possible are found in the literature previous to the work of H. Rose.[13] There are various known methods in which the precipitability of titanium from acid solutions by hydrolysis as metatitanic acid is used for the separation of titanium oxide from iron, aluminum and other metals yet all lack quantitative data on acid concentration; all involve the hydrolysis of very dilute solutions, as previously mentioned; or are concerned with the hydrolysis of a chloride solution, free from sulphates;[14] or of titanic acetate as in the well known method of Gooch for separating titanium and aluminum;[15] or hydrolysis of a titanium sulphate solution in the presence of sodium thiosulphate, the thiosulphate reducing the iron to the ferrous condition by reason of the sulphurous acid formed as a product of its decomposition;[16] or the hydrolysis of a sulphate solution under hydrogen sulphide to precipitate titanium oxide free from iron.[17]

However, L. Levy showed the following results on boiling titanium sulphate solutions for six hours:

Grams per 100 cc.					
free H_2SO_4	0.000	0.083	0.500	1.000	5.766
TiO_2 used	0.086	0.086	0.086	0.082	0.030
TiO_2pptd.	0.047	0.036	0.085	0.080	0.000

Hence, if too much sulphuric acid be present, the titanium dioxide will be imperfectly precipitated.[18]

L. Kayser[19] reports a study on the hydrolysis of titanic sulphate solutions as a basis for the separation of titanium and aluminum. As in all quantitative work on the hydrolysis of titanium

solutions the concentrations studied by L. Kayser are too dilute to be of industrial interest, but inasmuch as his work is the most complete paper on hydrolysis of titanium solutions reported in the literature his results are given here in some detail. Conductivity measurements were made, at 25° C., on titanium sulphate solutions of 0.01, 0.02, and 0.05 mol concentrations over a period of time. Kayser found that with increasing content of titanium oxide and decreasing pH the average increase of conductivity with time is more regular, the conductivity curve steeper and the final value is therefore reached later; with increasing content of titanium oxide at constant pH the increase in conductivity is greater and the final value is reached still later. A separate addition of sulphuric acid to pure titanium sulphate solutions causes the conductivity to decrease to a minimum and from there to increase very slowly. The formation of slowly hydrolyzed complex titanium sulphates may be regarded as a basis for this phenomenon. Kayser states: "It seems clear, and is confirmed by observation that, taken individually, the progress of the slow hydrolysis (at room temperature) as measured by increase in conductivity is limited by the changing of the degree of dispersion of the stable phase which is precipitated. It can be assumed that owing to changing of the degree of dispersion in such solutions the adsorbing power of the colloidal phase on the one hand and solubility, due to the increase in size of the particles, on the other hand, are decreased. The first causes an increase in the concentration of the two free hydrolysis products, the latter a limiting of the reverse reaction. Both processes proceed and cause the increase in conductivity the changing course of which (in the titanium sulphate solutions measured first a faster, then a slower rise) may be traced back to the more or less strong preponderance of one or the other influence. Particularly in the case of titanium sulphate the thing that influences the increase in conductivity may be that the stable hydrolysis product is not pure metatitanic acid but contains basic sulphate. This is also slowly decomposed by water." Kayser also found that the increase in conductivity was not accompanied by a corresponding increase in acid concentration (decrease in pH). In explanation he states: "According to experiments on the temporary pH change of solutions, in those in which titanium is understood to be in solution, it is to be assumed that all fresh titanium solutions are already hydrolyzed to a great extent. If it is assumed, therefore, that a highly dispersed phase is formed by this true hy-

drolysis and that the increase in conductivity depends solely on the increase in concentration of free acid, the order of magnitude of the increase in conductivity and the difference in pH are brought more nearly correct in relation; the specific conductivity behaves like the H-ion concentration.—The increase in concentration of free hydrogen ions in the titanium sulphate solutions seemed so small that one could not explain by it alone the above assumptions for increase in conductivity. The possibility of an explanation is found, if the specific properties of the adsorbing media are taken into consideration. This is in this case a most highly dispersed phase of titanium oxyhydrate that is so finely divided that it cannot be recognized as a colloid by the usual methods. Possibly the adsorbed hydrogen ions take part in the electrolytic conductivity, however their being carried with the adsorbent lessens the mobility of the ions, thus explaining the small conductivity in the beginning."

While the practical application of the hydrolysis of titanium sulphate solutions for the industrial large-scale production of titanium oxide, or more exactly hydrated titanium oxide which is calcined to produce the oxide, may be found in the patent literature very little fundamental information is contained therein.

A. J. Rossi and L. E. Barton[20] describe the hydrolysis of titanic sulphate solutions which contain 0.5-3 per cent of titanium oxide and about 0.15-0.2 per cent of free sulphuric acid. The product obtained by boiling such a solution is called a basic titanium sulphate and contains titanium oxide 70-80 per cent, sulphuric anhydride 5-10 per cent, and combined water 15-20 per cent. They state that the composition of the product will vary a little depending on conditions of precipitation, particularly as regards the titanium oxide and free acid concentration of the solution; excessive dilution yielding products lower in surphuric anhydride.

L. E. Barton[21] treats a titanium sulphate solution containing about 11 per cent of titanium oxide and no free sulphuric acid with lime equivalent to 20 per cent of the total acid. The calcium sulphate formed is filtered out and the solution is diluted so as to contain about 3 per cent of titanium oxide. This solution is then heated, while being electrolyzed, to precipitate titanium oxide. He states that in actual operations there have been thus obtained yields in precipitates of from 85-95 per cent of the total titanic oxide in the solution, in from two and a half to five hours.

M. Fladmark[22] states that precipitation of titanium hydrates from aqueous solutions is thought to depend upon the hydrolytic decomposition of the titanium salts resulting in a complete or partly colloidal solution of the titanium hydrates. The precipitation is then based upon the fact that the colloidal titanium hydroxide is caused to coagulate, whereby it is precipitated in a comparatively insoluble condition. As a result the hydrolytic equilibrium is disturbed and a new quantity of colloidal titanium hydroxide is produced by decomposition of the remaining titanium salts. This new quantity of hydroxide is again coagulated and so on. Solutions of 80-350 grams titanium oxide per liter and from 82-410 grams per liter of sulphuric acid not bound to other ions than titanium are convenient. Precipitates obtained from such solutions show 15 to 25 per cent combined water, 3-7 per cent sulphuric anhydride, from a trace to 2 per cent ferrous oxide, and the remainder as titanium oxide.

J. Blumenfeld[23] describes the preparation of a titanium sulphate solution containing 15-25 per cent titanium oxide. Such a solution on being heated below the boiling point, 95-130°C., precipitates titanyl sulphate $TiOSO_4 \cdot 2H_2O$, in the form of needle-like microscopic crystals.

P. Farup[24] claims that the rate of hydrolysis is markedly increased by the presence of previously precipitated finely divided metatitanic acid and describes a process wherein a solution containing 9.1 per cent titanium oxide, 10.9 per cent ferrous oxide, 30.2 per cent sulphuric anhydride and 1.5 grams per liter titanium oxide as titanous sulphate is run into a solution, maintained at the precipitation temperature, containing 8.2 per cent precipitated titanium oxide, 0.9 per cent titanium oxide in solution, 10.9 per cent ferrous oxide and 20.5 per cent free sulphuric acid.

W. Mecklenburg[25] states that whenever titanium salt solutions are subjected to hydrolysis, a certain "lag" or induction period is observed between the commencement of the operation and the first visible precipitation, and it is believed that during this induction period, colloidal particles of hydrated titanium oxide form in the solution which particles serve as centers for the accumulation of additional hydrolyzed particles and result in the formation of aggregates which produce a visible precipitate. In support of this he found that if titanium hydroxide was precipitated by neutralization of a solution with sodium hydroxide and a small amount of

the suspension was added to a hydrolyzable titanium solution, the mixture appeared turbid until the temperature had been raised above 50-60°C. At about this temperature the turbidity disappeared. When heated at about 100-105°C. for three hours, the titanium oxide was almost entirely precipitated, the yield being in excess of 95 per cent. Under the same conditions, an unseeded solution yielded no more than 35-70 per cent titanium oxide. As little as 1 per cent of seed (based on the weight of seed titanium oxide as compared to the precipitated titanium oxide) was sufficient to produce the result. Mecklenburg believes that the titanium hydroxide added is not actually dissolved on heating but is converted to some colloidal form which promotes the hydrolysis of titanium sulphate solutions. In contradistinction to P. Farup[24] he found that the addition of metatitanic acid does not hasten the hydrolysis.

Similarly J. Blumenfeld[26] claims a marked increase in the rate of hydrolysis if it is carried out in the presence of some titanium oxide in the colloidal form. It is worth noting that Blumenfeld states that the precise chemical linkage of the titanium and sulphuric acid is not completely understood; titanyl sulphate, $TiOSO_4 . 2H_2O$, may be crystallized under certain conditions; but at the same time some persons are of the opinion that titanium is present in solution as the normal sulphate. Whatever the exact chemical composition may be, the fact is that the final equilibrium of such solutions is directly proportional to the concentration of the sulphate and titanium oxide ions present. He obtains colloidal titanium by pouring a concentrated titanium solution into boiling water during a definite time period. He finds that high acid concentrations favor high yields of precipitated titanium oxide. Also that high speeds of mixing the concentrated titanium solution with the hot water give lower yield and incomplete precipitation, due to the fact that an adequate colloidal phase is not formed; and that if the solution is added at a speed less than an optimum, there is a gradual diminution in yield.

As for the composition of the product of thermal hydrolysis, this varies rather widely with the conditions of hydrolysis. Thus A. J. Rossi and L. E. Barton[20] give as the analysis of their product: titanium oxide 70-80 per cent, sulphuric anhydride 5-10 per cent, and combined water 15-20 per cent; with the general statement, as previously noted, that excessive dilution during hydrolysis

yields products lower in sulphuric anhydride. Demoly[27] dried metatitanic acid in vacuum and at 140°C. to constant weight and then ignited with a loss of 12.25 per cent water. He therefore assigned the formula $3TiO_2 . 2H_2O$ to metatitanic acid. V. Merz[17] found the water content of the meta acid to vary quite widely with the method of drying. Tuttschew[28] claimed the normal hydrate to be $TiO_2 . 2H_2O$; with the same loss on ignition whether the titanic acid be prepared from the chloride or sulphate. However, as previously noted Carnelly and Walker[11] state that titanic acid does not form any definite hydrates. Outside the patent literature there does not seem to have been any recognition of the sulphuric anhydride content of the product obtained by thermal precipitation of hydrated titanium oxide from titanium sulphate solutions nor that such may be a component part of the molecule, *i. e.*, the product precipitated may be a basic sulphate as claimed by Rossi and Barton[20] or a mixture of metatitanic acid and basic titanium sulphate.

A survey of the literature has shown, then, that quantitative information on the thermal hydrolysis of pure titanium sulphate solutions has not been hitherto published. It was therefore planned to prepare iron-free solutions of titanium sulphate varying in concentration from 1-10 per cent of titanium oxide by weight and of selected acid concentrations, to hydrolyze these solutions by boiling, or heating at 100°C. and to observe, analytically, the progress of the precipitation. The results of these observations together with determinations of the densities of certain of these solutions and analyses of a few of the precipitation products are recorded in the following pages.

EXPERIMENTAL.

Chemicals.

All chemicals used were the best "c.p.", reagent grade chemicals obtainable, with the exception of titanium sulphate which was prepared in this laboratory.

Distilled water was used throughout.

Iron free titanium sulphate is not commercially available. The so-called c.p. titanium sulphate imported by chemical supply companies has an appreciable iron content and is not completely soluble.

It was therefore necessary to prepare iron free titanium sulphate in this laboratory. Crude titanium sulphate, $Ti(SO_4)_2 . 9H_2O$, is prepared in the United States, but was not used as a source for the preparation of pure titanium sulphate because of its phospate content which is difficult to remove. Titanium tetrachloride was used as the starting material. This was once re-distilled, 134-138°C. About 400 cc. of the titanium tetrachloride were dissolved in 1400 cc. of water. The resulting solution of titanium tetrachloride was reduced by means of stick zinc to a light brown color, and 100 cc. were further reduced to a deep violet color. The solution was reduced until distinctly colored by the presence of titanous ion in order to insure that all the iron present was in the ferrous state to prevent hydrolysis and precipitation of ferric iron with the titanium. Dilute oxalic acid solution also prevents precipitation of any iron with the titanium.[29] The highly reduced titanium tetrachloride solution was added drop by drop to a boiling solution of 10 grams of oxalic acid in 10,000 cc. of water contained in a round-bottom flask. Then 800 cc. of the lightly reduced solution were added drop-wise. Boiling was continued for a total period of six hours, hot water being added from time to time to maintain constant volume. These precipitation conditions were arrived at after very considerable experimentation. Comparatively small changes in initial concentration of titanium or oxalic acid, or too rapid addition of the titanium tetrachloride to the boiling solution, or change in the total volume result in the precipitation of a colloidal unfilterable form of metatitanic acid. The precipitate of metatitanic acid, obtained as described, was filtered on several large Buchner funnels and washed with boiling hot water until the washings were free from chloride. The precipitate was sucked dry, transferred to a beaker, and about one and a quarter times its weight of concentrated sulphuric acid added. The mixture was gently boiled until crystallization of the mass took place. After cooling, an equal weight of water was added and the whole allowed to stand for several days with occasional stirring. The resulting solution was clarified by filtration with Super-Cel which had been previously washed free from iron with hot hydrochloric acid and then free from chloride with hot water. The solution so prepared was free from iron (ammonium thiocyanate test) and chloride (silver nitrate test). Portions of this solution were then concentrated to 15-18 per cent titanium oxide by evaporation below 60°C. under reduced pressure. A

typical solution so obtained was one containing 15.85 per cent titanium oxide and 20.96 per cent free sulphuric acid by weight. Such solutions were not stable; a water-soluble titanium salt crystallizing out on standing. Analysis of this crystalline material proved it to be the basic sulphate dihydrate, $TiOSO_4 . 2H_2O$. Analysis:*

	found	calculated
TiO_2	40.86%	40.83%
SO_3	40.51	40.81

This solution was therefore crystallized by heating at 100°C. for 24 hours, and the crystalline basic titanium sulphate thus obtained dissolved in water. It may be noted that the compound which was crystallized is peculiar in that it dissolves very slowly in water, sometimes 24 hours being required to obtain complete solution in an equal weight of water. The solutions were then analyzed and adjusted to the desired maximum titanium oxide concentration by evaporation under reduced pressure, and sulphuric acid added to obtain the desired acidity. As may be readily recognized, it was necessary to make a number of adjustments in order to obtain simultaneously predetermined titanium oxide and sulphuric acid concentrations.

ANALYTICAL METHODS.

Titanium sulphate solutions.

Gravimetric estimation of titanium oxide.[30] The solution of the titanic salt contained a sufficient quantity of free mineral acid in the volume employed to prevent the precipitation of titanium on boiling. The solution, occupying a volume of 300-400 cc., was heated to the boiling point, the flame removed just long enough for the liquid to become calm and the titanium thrown down by the gradual addition of pure ammonium hydroxide in excess. The liquid was heated and stirred for a few minutes to coagulate the precipitate; when it was allowed to stand until the titanic acid had subsided. The precipitate was collected on an ashless filter paper and washed with hot water. While still moist,

* A spectroscopic analysis by Prof. H. T. Beans and Dr. A. Dingwall of Columbia University showed the presence of no other recognizable elements indicating that the method of preparation used produced a product of exceptional purity.

the filter with its contents was placed in a tared platinum crucible, carefully dried, the paper smoked off, the residual carbon burned away and the crucible finally brought to constant weight over the Meker burner.

Volumetric estimation of titanium oxide (method of the Titanium Pigment Company, Inc.). This method was used for most of the estimations of titanium oxide in this work. The gravimetric method was used only where so designated.

Reagents: Standard ferric ammonium sulphate. Thirty grams of ferric ammonium sulphate, $Fe_2(SO_4)_3 . (NH_4)_2SO_4 . 24H_2O$, were dissolved in about 300 cc. of water acidified with 15 cc. of concentrated sulphuric acid; heated to above 60° C. and 0.1 normal potassium permanganate added drop by drop with stirring until the solution was just colored pink, in order to oxidize any ferrous iron present to the ferric condition. The solution was cooled to room temperature and diluted to one liter. This solution was then standardized in terms of iron by passing through a reductor slowly, as specified in the method for titanium, and titrated with a standard potassium permanganate solution whose iron value was previously ascertained by standardization against sodium oxalate. The iron value multiplied by the factor 1.4344 equaled the titanium oxide value.

Indicator. Saturated aqueous solution of potassium thiocyanate.

Reductor. The Jones reductor used for titanium reduction was a 1000 cc. burette, 2 inch inside diameter and 22 inches long above the stop-cock. The stem below the stop-cock was ¼ inch inside diameter and 3½ inches long. The reductor was charged with about 1000 grams of amalgamated zinc (equal weights of 10 and 20 mesh zinc mixed), supported on a one inch mat of glass wool. About 500 grams of amalgamated stick zinc were added on top of the mesh zinc in sticks about 2½ inches long and of ¼ inch diameter. Enough mesh zinc was used to make a column of 6 inches in height and the stick zinc increased the height to about 12 inches. To amalgamate the zinc 11 grams of mercuric chloride were dissolved in 100 cc. of hydrochloric acid, sp. gr. 1.20. About 250 grams of zinc were just covered with distilled water in a heavy-walled liter flask and the mercuric chloride slowly poured in with shaking. The mixture was shaken for about two minutes.

The solution was poured off and the amalgamated zinc washed thoroughly with hot water. Each day immediately before it was used the zinc in the reductor was cleaned by washing with hot sulphuric acid, and rinsed with hot distilled water. In draining and washing the reductor, the liquid level was at no time allowed to go below the top of the mesh zinc layer. When it was not in use the zinc in the reductor was kept covered with distilled water, and a beaker over the top of the reductor excluded dust.

Estimation of titanium oxide. The titanic sulphate solution, containing not more than 250 milligrams of titanium oxide in 150 cc. of a 20% by volume sulphuric acid solution, was heated to boiling and then transferred to a clean reductor which had been previously heated with hot distilled water, and allowed to remain 15-20 minutes. The solution was then drained (not allowing the liquid level to go below the top of the mesh zinc) into a one liter Florence flask containing 5 cc. of a saturated solution of potassium thiocyanate, and which had been swept out with carbon dioxide gas. Carbon dioxide gas was continuously passed through the flask during the draining and washing process. The reductor was washed once with hot sulphuric acid (1:5), and three times with boiling water. The reduced solution was immediately and rapidly titrated with the standard ferric ammonium sulphate solution to a permanent faint yellowish color.

Volumetric estimation of sulphuric acid. The total sulphuric acid in the titanium sulphate solutions was determined by titration with a 0.5 normal solution of sodium hydroxide which had been standardized against benzoic acid. Methyl orange was used as the indicator. To avoid difficulty in recognizing the end-point of the titration, a dilution of titanium was used which did not precipitate too great a quantity of orthotitanic acid. A spot plate was occasionally used in obtaining a better end-point. Equivalent sulphuric acid was calculated as equivalent to the titanium oxide as titanic sulphate $Ti(SO_4)_2$. The titanium precipitated as orthotitanic acid, $Ti(OH)_4$, during the titration. The difference between the total and equivalent acid is hereafter designated as excess sulphuric acid.

Hydrolytic products.

In those cases in which an analysis of the hydrolytic products was made the precipitate was collected on a Buchner funnel, washed free of titanium with dilute sulphuric acid and then with water

until the washings were neutral to litmus. The precipitates were then air-dried for a week, powdered and allowed to dry two more days after which they were kept in well corked test-tubes.

Estimation of uncombined water.

A weighed air-dried sample was dried in a Freas oven at 105°C. to constant weight. The loss in weight was taken as uncombined water.

Estimation of titanium oxide.

A 250 milligram sample was weighed, transferred to a 250 cc. beaker, and 25 cc. of concentrated sulphuric acid and 10 grams of ammonium sulphate added. This was boiled until a clear solution was obtained, allowed to cool, then diluted with 100 cc. of water and the titanium oxide estimated by reduction and titration as described in the analysis of titanium sulphate solutions.

Estimation of sulphuric anhydride.

A 0.5 gram sample was weighed into a platinum crucible, 10 grams of anhydrous (sulphate free) sodium carbonate added, and the mixture fused until a clear melt was obtained. The melt was digested in about 100 cc. of water until thoroughly broken down, filtered and washed seven times with hot 5 per cent sodium carbonate solution, and the washings combined with the filtrate. The solution was acidified with concentrated hydrochloric acid, carbon dioxide boiled out, and if necessary additional hydrochloric acid was added to acidify. The sulphuric anhydride was then determined by precipitation as barium sulphate.[31]

Estimation of combined water.

A weighed sample, dried at 105°C., was ignited over the Meker burner to constant weight. The sulphuric anhydride in the ignited residue was then determined according to the method immediately above. The loss in weight on ignition, less the sulphuric anhydride lost on ignition, i. e., the difference between the total sulphuric anhydride and that remaining in the ignited residue, is designated as combined water.

It must be recognized that this method of analysis of the hydrolysis products is empirical. However, it was thought that analyses of the various hydrolytic products would be comparable and that differences in these products would be sufficiently indicated.

The weights used were calibrated by the method of T. W. Richards.[32].

Burettes were calibrated by means of a Kiehl calibrating pipette.

METHOD OF PRECIPITATION.

The titanium sulphate solutions were precipitated by boiling in a three-necked round bottom 500 cc. flask. The center neck of the flask was attached to a water-cooled condenser. A mechanical stirrer extended through the condenser and into the flask. The stirrer prevented bumping, and the reflux condenser permitted the boiling of the solution at atmospheric pressure without changes in concentration due to evaporation. The side necks of the flasks were used to hold a thermometer and to facilitate the removal of samples, respectively. A bank of ten such set-ups was used.

About 250 cc. of titanium sulphate solution of known concentration of titanium oxide and sulphuric acid to be hydrolyzed was placed in the flask, mounted under the reflux condenser, agitation started and rapidly heated to the boiling point. After boiling gently a definite time, the flame was removed and agitation stopped. When sufficiently cooled to permit removal of a sample without appreciable loss of water vapor, a sample was withdrawn by means of a pipette. The flask was then re-stoppered, agitation renewed, rapidly heated to the boiling point again, and gently boiled for the given time period as before. The precipitations were made in this manner over a total boiling period of eight hours, and a sample removed at the end of each hour.

EXPERIMENTAL RESULTS AND DISCUSSION.

Titanium Sulphate Solutions, Acidity Factor 0.5.

The first solutions to be considered here were solutions varying from about one per cent to about ten per cent of titanium oxide by weight, at approximately one per cent intervals, with an acidity factor 0.5. By acidity factor is meant the ratio of the concentration of excess sulphuric acid to the concentration of titanium oxide present in the solution, e.g., a solution containing ten per cent titanium oxide and five per cent excess sulphuric acid has an acidity factor of 0.5. Excess sulphuric acid is here considered to be

the sulphuric acid in excess of that equivalent to the titanium as titanic sulphate, $Ti(SO_4)_2$.

A titanium sulphate solution was prepared as has been previously described. This solution analyzed:

	per cent by weight	grams per liter
titanium oxide	9.91	137.12
total sulphuric acid	29.43	407.76
equivalent acid	24.27	335.9
excess acid	5.16	71.8
acidity factor	0.52	

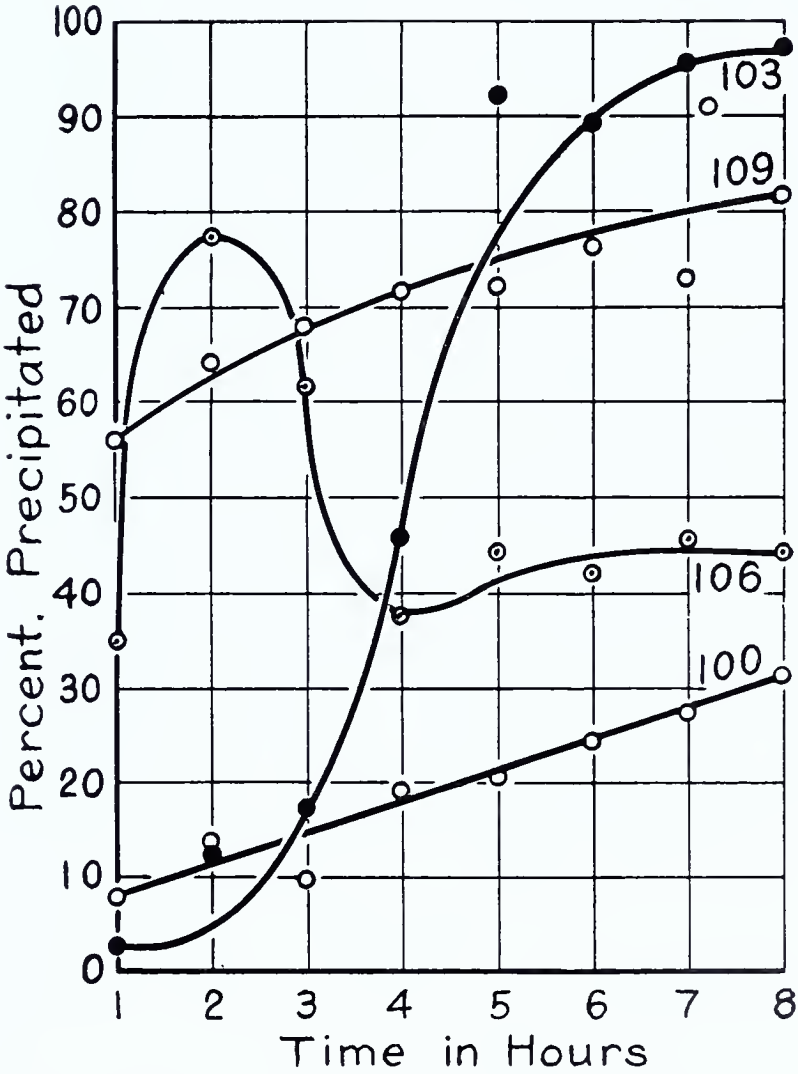
Ten dilutions of this solution were prepared containing titanium oxide from about 10 to 1 per cent by weight. They were diluted with distilled water so that the acidity factor remained constant through the series. (A series of ten solutions diluted in this way from a concentrated solution with an acidity factor of 2.1 showed on analysis an average deviation of 0.02. This deviation was not considered significant.)

A sample of each dilution thus prepared was retained for analysis and the bulk of the solutions immediately hydrolyzed by boiling as described. The analyses of these original solutions are given in Table 1. Samples were withdrawn at the end of hourly boiling periods, with a total boiling time of eight hours. These withdrawn samples were decanted or filtered and the solution analyzed for titanium oxide content by reduction and titration against standard ferric alum solution as has been previously described. The difference between the titanium oxide concentration of an original solution and that in a sample withdrawn at the end of a given hydrolysis period represents the amount of titanium oxide precipitated in that time. The per cent precipitated is one hundred times the ratio of titanium oxide precipitated to the titanium oxide originally present in a given volume of solution. The results obtained are summarized in Table 2 and Figures 1 and 2.

Table 1.

Series I. Titanium sulphate solutions, acidity factor 0.5; concentrations of titanium oxide.

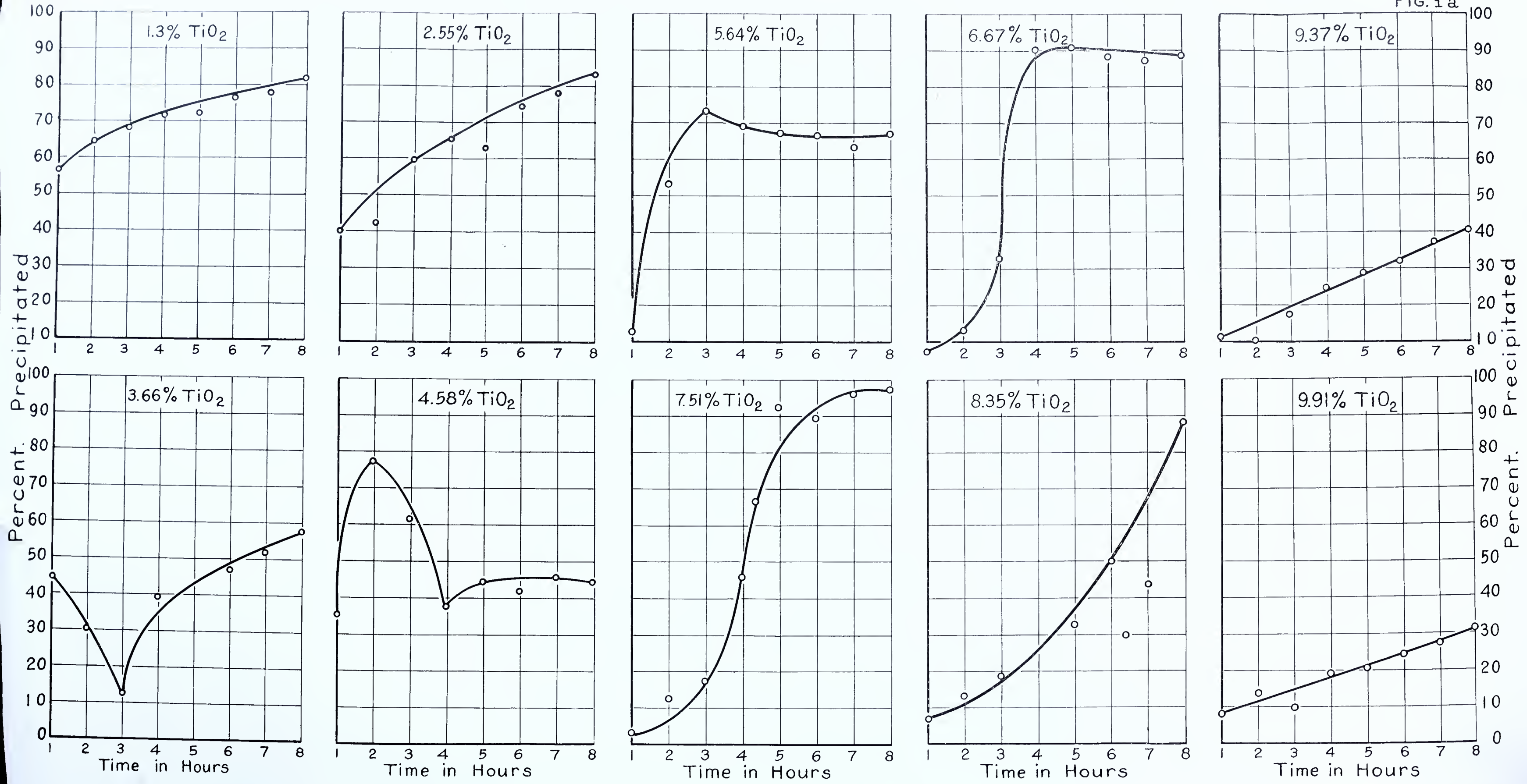
No.	Per Cent by weight	Grams per 100 cc.
100	9.91	13.72
101	9.374	12.21
102	8.347	10.76
103	7.513	9.435
104	6.665	8.139
105	5.636	6.692
106	4.576	5.366
107	3.656	4.076
108	2.545	2.737
109	1.318	1.436



100—9.91% titanium oxide 106—4.58% titanium oxide
103—7.51% " " 109—1.32% " "

Figure 1. Influence of length of hydrolysis period on the per cent precipitated; titanium sulphate solutions, acidity factor 0.52.

FIG. 1a


1.3% TiO_2
2.55% TiO_2
5.64% TiO_2
6.67% TiO_2
9.37% TiO_2
3.66% TiO_2
4.58% TiO_2
7.51% TiO_2
8.35% TiO_2
9.91% TiO_2
Percent. Precipitated
Time in Hours

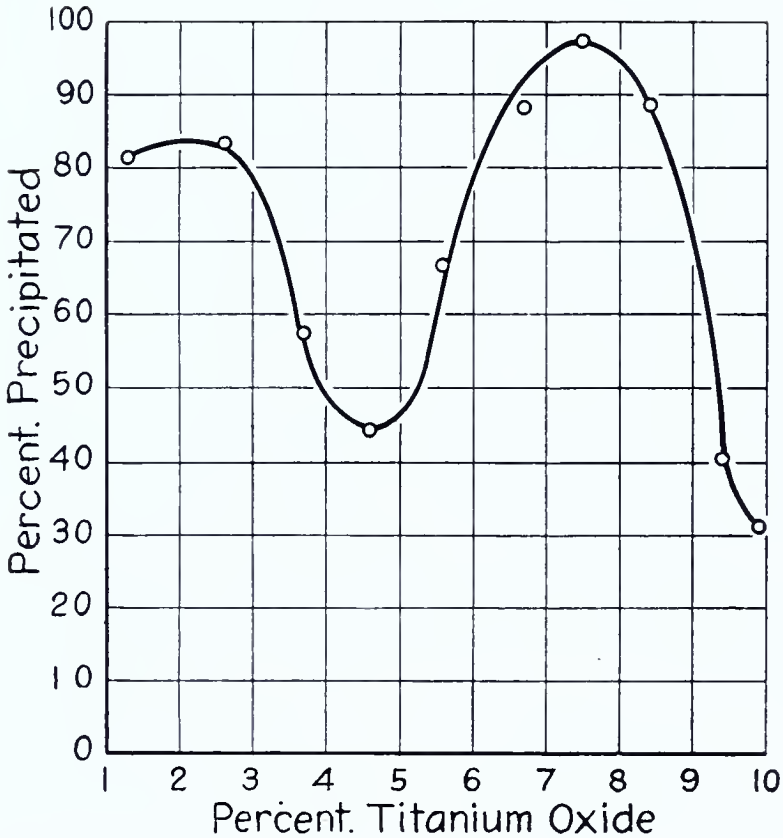


Figure 2. Influence of titanium oxide concentration on the per cent precipitated in eight hours at the boiling point; titanium sulphate solutions, acidity factor 0.52.

Figures 1 and 2 are plotted from the data of Table 2. In Figure 1 in which the per cent precipitated is plotted against the time during which hydrolysis has proceeded at the boiling point, only representative curves are plotted in order to avoid the confusion which would arise if it was attempted to plot all the data on a single graph. Inasmuch as typical curves have been selected it is not necessary to plot all the data.

Table 2.

Precipitation of Titanium Sulphate Solutions, Acidity Factor 0.52.

Soln. No.	Original concentration Per cent by vol.	Per cent TiO_2 by volume 1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.	8 hrs.
100	13.72	12.59	11.82	12.36	11.09	10.92	10.39	9.95	9.41
101	12.21	10.85	10.97	10.07	9.16	8.68	8.40	7.68	7.27
102	10.76	10.01	9.30	8.71	8.05	7.21	5.34	6.03	1.24
103	9.44	9.16	8.25	7.78	5.10	0.724	0.980	0.374	0.253
104	8.14	7.51	7.02	5.46	0.784	0.731	0.910	1.01	0.935
105	6.69	5.82	3.11	1.76	1.96	2.19	2.24	2.24	2.22
106	5.37	3.47	1.21	2.04	3.33	2.98	3.11	2.97	2.98
107	4.08	2.28	2.85	3.56	2.48	2.23	2.17	1.96	1.73
108	2.74	1.54	1.28	1.10	0.953	1.01	0.696	0.585	0.458
109	1.44	0.599	0.491	0.440	0.398	0.380	0.322	0.359	0.250

Soln. No.	Original concentration Per cent by wt.	Per cent precipitated 1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.	8 hrs.
100	9.91	8.24	13.85	9.92	19.18	20.42	24.28	27.47	31.43
101	9.37	11.14	10.16	17.53	24.90	28.91	32.03	37.11	40.46
102	8.35	6.99	13.59	19.04	25.28	33.08	50.36	43.95	88.46
103	7.51	2.92	12.52	17.57	46.00	92.33	89.61	96.04	97.32
104	6.67	7.79	13.77	32.96	90.37	91.02	88.82	87.63	88.51
105	5.64	13.03	53.60	73.64	69.25	67.26	66.48	63.51	66.89
106	4.58	35.39	77.53	61.91	37.98	44.50	42.03	45.77	44.39
107	3.66	44.16	30.11	12.74	39.23	45.42	46.84	51.94	57.56
108	2.55	46.91	42.17	59.92	65.18	63.10	74.57	78.62	83.26
109	1.32	56.29	64.23	67.95	71.70	72.33	76.48	73.86	81.80

The course of precipitation over a given period of time varied with different concentrations of titanium oxide. However, the concentrations selected were such that two or more of the solutions used always fell within a concentration range which had a specific effect upon the course of precipitation, i. e., the precipitation-time curves are more or less parallel. In plotting the data a typical curve in each concentration range was selected. For example, in Figure 1, curve 100 is plotted from data on the 9.91 per cent titanium oxide solution and is also typical of the course of precipitation of the 9.4 per cent titanium oxide solution; curve 103 shows the characteristic precipitation of solutions of 6.7-8.3 per cent titanium oxide; curve 106 is typical of solutions of 3.7-5.6 per cent titanium oxide; and curve 109 is the type which occurs with solutions of 1.3-2.5 per cent titanium oxide. It must be noted that there is no sharp differentiation between these curves; a gradual change taking place from one type to another. This is not shown in Figure 1 since typical curves are given and the transition curves omitted. In Figure 1a the individual curves for this series have been plotted in order to show more clearly the change in form of the curves with change in the titanium oxide concentration.

The effect of a specific range of concentration upon the course of precipitation is also evidenced by change in direction of the precipitation-concentration curve (Figure 2). The concentrations of titanium oxide used as showing a typical course of hydrolysis with time were also those which fall at maximum or minimum points in the curve showing the influence of concentration upon the extent of precipitation after eight hours of boiling, and the highest and lowest concentrations used. In Figure 2 the per cent of titanium oxide precipitated, at the end of eight hours of boiling, is plotted against the titanium oxide concentration.

It is apparent from Figure 1 that precipitation proceeds at very different rates at various titanium oxide concentrations, and that the direction of the precipitation-time curves varies widely at the different titanium oxide concentrations. In the most dilute and in the most concentrated of the solutions studied, i. e., titanium oxide concentrations of 1.3 to 2.5 per cent and 9.4 to 9.9 per cent by weight, respectively, the rate of precipitation, after the first hour of boiling, was approximately constant up to the end of at least eight hours. However, during the first hour of boiling very much more precipitation occurred in the dilute solutions than in

the concentrated solutions. A very considerable portion of this difference no doubt is due to hydrolysis which has taken place at room temperature on preparation of the solution. Disregarding hydrated forms, the titanium may be in the form of titanic sulphate, $Ti(SO_4)_2$, or titanyl sulphate, $TiOSO_4$. Both of these compounds are known but as to which form, if either or both, is present in sulphuric acid solutions of titanium is not known. It might be expected that in more dilute solutions the basic sulphate or even more basic forms, $Ti(OH)_2SO_4$ for example, or rather the ions of these compounds would predominate and that therefore the initial precipitation at elevated temperatures would be more rapid. It is well known that dilute titanium solutions of relatively low acidity hydrolyze and deposit hydrated titanium oxide even at room temperature.

The course of precipitation of the 7.5 per cent titanium oxide solution is shown in curve 103 of Figure 1. There was apparently at first a "lag" or induction period up to the third hour of boiling during which precipitation proceeded comparatively slowly, the per cent precipitated rising to only 18 per cent. During the next three hours the precipitation was the most rapid, the per cent precipitated rising from 18 to 90 per cent. Finally during the last two hours observed the precipitation again proceeded rather slowly, only 7 per cent more of the titanium oxide being precipitated in the two hours. This final decrease in the rate of precipitation was to be expected, inasmuch as the concentration of titanium in solution has been greatly reduced and in addition the free acidity of the solution has been raised due to the liberation of combined sulphuric acid. It is in this concentration that maximum precipitation in the eight hour period occurred.

The precipitation of the 4.6 per cent titanium oxide solution (curve 106, Figure 1) was peculiar in that after the second hour of boiling the hydrated titanium oxide which had been precipitated apparently re-dissolved until the fifth hour after which the per cent precipitated remained very nearly constant. It may also be especially noted that in the series of solutions with titanium oxide concentrations ranging from 1.3 to 8.3 per cent, a minimum in the precipitation-concentration curve occurs in this solution with a concentration of 4.58 per cent titanium oxide.

While in the above the course of precipitation has been described as occurring in four typical ways it seems reasonable to

suppose that in all concentrations studied there probably is at first an induction period of greater or less length, depending upon the titanium and acid concentration, during which nuclei or centers of precipitation form, this is then followed by a period of comparatively rapid precipitation, and finally the precipitation rate becomes relatively slow, and the reaction gradually approaches equilibrium.

The per cent precipitated at the end of eight hours did not have any direct relationship to the titanium oxide concentration of the original solution (Figure 2). With increasing titanium oxide concentration above 2.5 per cent, there was a decrease in the per cent precipitated until a concentration of 4.6 per cent titanium oxide was reached. At this point the per cent precipitated rapidly rose with increased concentration up to 7.5 per cent titanium oxide at which concentration optimum precipitation for the concentration range studied occurred; with further increase in titanium oxide concentration the per cent precipitated again decreased. This is contrary to what has been shown to be the case with other hydrolyzable salts. For example, Herz and Bulla[33] state: "The dependence of the hydrolytic precipitation of bismuth on the water concentration is unmistakable; the greater the amount of water the smaller is the amount of dissolved bismuth." Similarly, Kullgren[34] found that for most salts hydrolysis increases slowly with dilution. The salts used by Kullgren were aluminum chloride, nitrate and sulphate, mercuric chloride, copper chloride and nitrate, lead chloride and nitrate, ammonium chloride and nitrate, zinc chloride, nitrate and sulphate, cobalt chloride and nitrate, nickel chloride, cadmium chloride, manganese chloride, and magnesium chloride. However, Kolthoff[39] has pointed out that when amorphous precipitates form, the mass action law is not applicable. He also states that the solubility of the amorphous form, is not constant, but depends upon the state in which the amorphous form happens to be at a certain moment. The type of precipitation-concentration curve obtained here for hydrated titanium oxide may depend then upon the varying solubilities of the hydrated oxides precipitated under different conditions of concentration, recognizing also that the precipitation conditions, and therefore also the solubilities of the precipitated products, are varying continuously during the hydrolysis period.

The observation that the optimum precipitation of titanium sulphate solutions of acidity factor 0.5 occurred at a titanium oxide

concentration of 7.5 per cent by weight may be of considerable practical interest. It is evidently unnecessary as well as undesirable to excessively dilute such solutions to obtain good precipitation within a reasonable period of time (in the industry a yield of 90-95 per cent is considered as quite satisfactory).

For time periods of less than eight hours similar curves are obtained, but the marked minimum and maximum are not as sharply defined. The concentration of the solution in which maximum precipitation occurred varied with the length of the hydrolysis period. The longer the period over which hydrolysis took place, the higher was the concentration of the solution in which maximum precipitation occurred. This is illustrated in Table 3 and Figure 3 using data selected from Table 2. The curve becomes flat, i. e., maximum precipitation did not occur in still greater concentrations with longer heating after six hours indicating that a longer heating period would not give maximum precipitation in still higher concentrations of titanium sulphate solutions of this acid content.

Table 3.

Optimum precipitation occurred in:

1 hr.	in the	soln.	of	1.3%	TiO_2	by	wt.
2 hrs.	"	"	"	"	4.6%	"	"	"
3 hrs.	"	"	"	"	5.6%	"	"	"
4 hrs.	"	"	"	"	6.7%	"	"	"
5 hrs.	"	"	"	"	6.7-7.5%	"	"	"
6 hrs.	"	"	"	"	7.5%	"	"	"
7 hrs.	"	"	"	"	7.5%	"	"	"
8 hrs.	"	"	"	"	7.5%	"	"	"

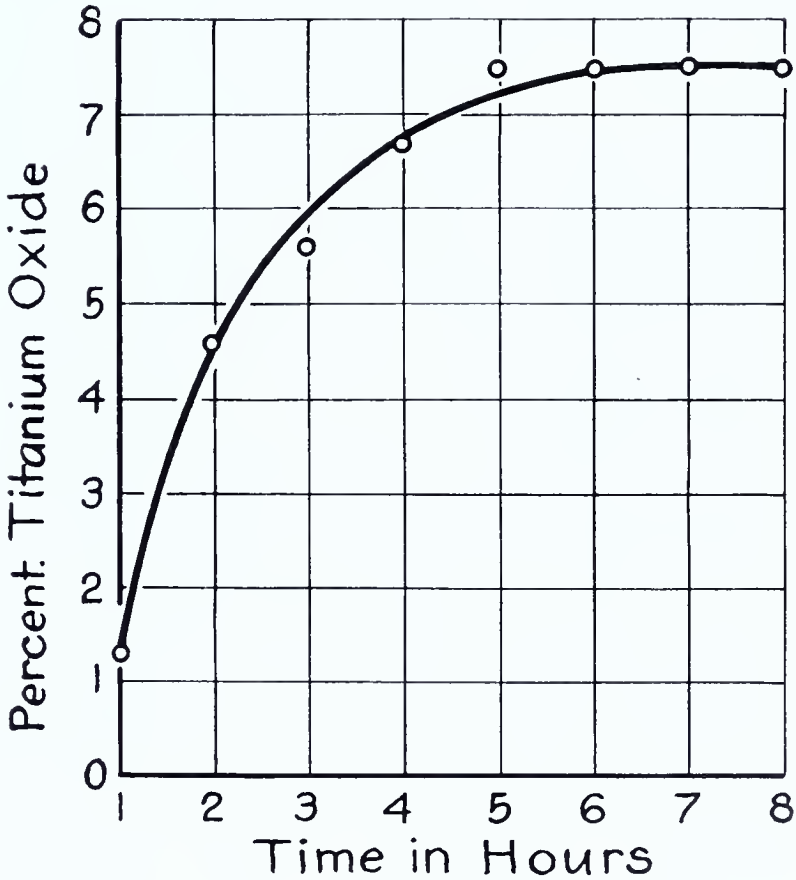


Figure 3. Influence of the length of hydrolysis period on the concentration in which maximum precipitation occurs; titanium sulphate solutions, acidity factor 0.52.

Since the precipitation did not decrease regularly with increasing concentration of titanium, it was suggested that the composition of the hydrolysis product might vary with the concentration of the solution from which it precipitated. If a more highly hydrated product were precipitated the supernatant solution would show a higher per cent concentration of titanium oxide because of the water held in the precipitate, etc. An attempt was made to determine the composition of the hydrolysis products by analysis. At the end of eight hours of boiling the precipitated hydrolytic products were separated from solutions 100 (originally 9.9 per cent titanium oxide), 103 (originally 7.5 per cent titanium oxide), 106 (originally 4.6 per cent titanium oxide) and 109 (originally 1.3 per cent titanium oxide), which concentrations showed maximum or minimum precipitation or were the highest or lowest concentration as the case might be, in the range studied. The precipitate in each case was collected on a Buchner funnel, washed free of titanium with dilute sulphuric acid and then with distilled water until the washings were free of acid (neutral to litmus). They were air-dried for a week, powdered and allowed to dry for two more days. Moisture was determined as the loss in weight on drying forty-eight hours at 105° C. The sulphate content was estimated by fusing with sodium carbonate, dissolving, filtering and precipitating the sulphate from the filtrate as barium sulphate which was separated, ignited and weighed. Combined water was determined by igniting the dried hydrolysis product and determining residual sulphate after ignition; the combined water then being the loss on ignition less the sulphuric anhydride lost on ignition. Titanium oxide was estimated by solution, reduction and titration with standard ferric alum solution. The results of these analyses are tabulated in Table 4. No correlation was found between the composition of the hydrolytic products and the concentration of the original solution from which they had been precipitated or the amount of hydrolysis which the solutions have undergone. It seems likely that the degree of hydration and combined sulphate of the original hydrolysis products may have been altered in washing them free of adhering solution. Hydrated titanium oxide precipitated from a titanium tetrachloride solution by boiling may readily be washed free of chloride with hot water; on the other hand, when a similar product prepared from a titanium sulphate solution is washed with hot water the sulphate is washed out very slowly and even after prolonged washing (for a week or

longer) small amounts of sulphate are present in the washings. Probably combined sulphate is gradually removed by continued washing. It may be noted, however, that the statement of A. J. Rossi and L. E. Barton[20] that excessive dilution during hydrolysis yields products lower in sulphuric anhydride is partially confirmed in that the sulphuric anhydride content increased with increasing dilution of the original solution, from 4.68 per cent sulphuric anhydride in the precipitate from the solution which originally contained 9.91 per cent titanium oxide, to 8.28 per cent sulphuric anhydride in the precipitate from the solution which originally contained 4.58 per cent titanium oxide; but the precipitated titanic acid from the lowest concentration (originally 1.32 per cent titanium oxide) shows a lowered sulphuric anhydride content, i. e., 6.00 per cent.

Table 4.

Analysis of Precipitation Products, Titanium Sulphate Solutions. Acidity Factor 0.5.

Soln.	TiO_2 % by wt. orig. soln.	% hyd. 8 hrs.	% Moisture	% TiO_2*	% SO_3*	% H_2O*	Total*
100	9.91	31.4	6.67	87.21	4.68	7.61	99.50
103	7.51	97.3	9.15	84.54	7.31	7.65	99.50
106	4.58	44.4	7.92	83.13	8.28	8.28	99.69
109	1.32	81.8	7.11	86.51	6.00	7.49	100.00

Deviation of the physical properties of a series of solutions from the law of mixtures may be indicative of chemical change. Dennison[35] states that if on the mixing of two substances no chemical reaction occurs, the mixture law holds for the physical properties of the mixture, i. e., the physical properties of a mixture are additive. He also showed that if any compound formation takes place on mixing, the deviation from the mixture law is proportional to the amount of compound formed. At any composition of the mixture at which the deviation becomes a maximum, the amount of compound formed must reach a maximum. If a chemical compound is formed the number of moles of compound is at a maximum when the mixture has the same composition as the compound, i. e., the maximum deviation of the property curve occurs at the composition of the mixture representing the formula of the compound. The position of the maximum in property-

* On dry basis.

composition curves shifts with changes in temperature. However, if the deviations of the property measured from that calculated according to the law of mixtures are plotted against the composition, the positions of the maxima are the same at all temperatures.

As previously noted, it is possible for the titanium in the solutions used to exist in various chemical combinations with the sulphuric acid and water present. Variations in the form of chemical combination, or the predominating form of combination, might account for the difference in the course of precipitation in the various dilutions which was observed. Measurement of the specific gravities of a series of solutions of different titanium oxide concentrations and a constant acidity factor of 0.5 was planned to determine whether the formation of compounds or hydrates in these solutions could be confirmed by maximum deviations in this physical property curve. A stock solution was prepared for these determinations which showed on analysis:

titanium oxide	9.87% by wt.
total sulphuric acid	29.29%
equivalent sulphuric acid	24.23%
excess sulphuric acid	5.06%
acidity factor	0.51

This solution was then diluted to the desired titanium concentrations. The titanium oxide concentrations were determined gravimetrically so as to insure the greatest possible accuracy. The specific gravity of each solution was determined by weighing in a 25 cc. glass stoppered Regnault pkynometer. (This was previously calibrated at the temperature to be used with triply-distilled water, prepared by redistilling distilled water once from alkaline permanganate and once from a dilute phosphoric acid solution through a block tin condenser.) The pyknometer full of the solution was placed in a thermostat at 25°C.±0.05° for two hours, the volume adjusted, and then weighed. The specific gravities and densities so obtained are given in Table 5.

Table 5.

Specific Gravity and Density of Titanium Sulphate Solutions, Acidity Factor 0.51.

Per cent TiO_2 by wt.	Specific Gravity	Density
9.909	1.3819	1.3774
9.176	1.3449	1.3409
8.374	1.3084	1.3045
7.530	1.2727	1.2689
6.670	1.2358	1.2321
5.750	1.1986	1.1950
4.737	1.1602	1.1568
3.65	1.1215	1.1181
2.49	1.0821	1.0788
1.29	1.0416	1.0385

In order to check these results and to secure more data a second series was run, adjusting the concentrations of titanium oxide so that they would fall between those of the above group. The same original solution, pyknometer bottles and thermostat were used. The values obtained are tabulated in Table 6.

Table 6.

Specific Gravity and Density of Titanium Sulphate Solutions, Acidity Factor 0.51.

Per cent TiO_2 by wt.	Specific Gravity	Density
9.909	1.3815	1.3774
9.504	1.3621	1.3580
8.767	1.3270	1.3230
7.965	1.2915	1.2876
7.112	1.2547	1.2509
6.204	1.2170	1.2133
5.230	1.1792	1.1757
4.224	1.1410	1.1376
3.04	1.1018	1.0985
1.88	1.0618	1.0566

In Figure 4 the specific gravity values are plotted as the ordinates and the titanium oxide concentrations of the solutions as the abscissae. The curve so obtained for the titanium sulphate solutions rises as a straight line from 1.3 per cent titanium oxide

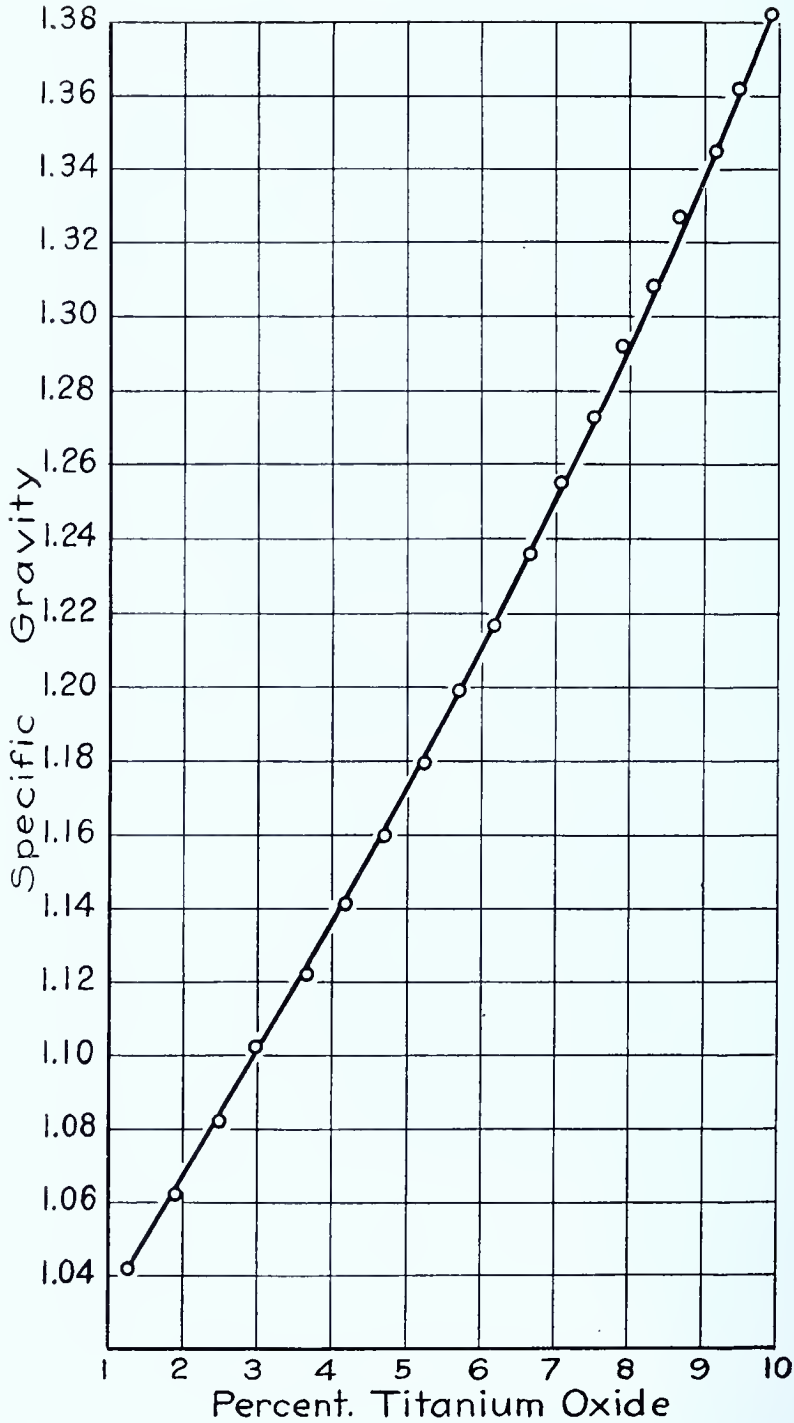


Figure 4. Specific gravity, at 25°C., of titanium sulphate solutions, acidity factor 0.51.

to 4 per cent titanium oxide and from that point the specific gravity increases more rapidly with increasing concentration as indicated in the figure. Such behaviour is to be expected as only in an ideal solution would the specific gravity-concentration curve continue as a straight line beyond the most dilute solutions.

The deviation of the density observed from that calculated according to the law of mixtures was determined using as the densities at 25° C. of the components:

titanium oxide	3.9
sulphuric acid	1.8255
water	0.9971

The densities of water and sulphuric acid were obtained from the International Critical Tables. The value of 3.9 for titanium oxide represents the average of many determinations made for the Titanium Pigment Company, Inc. Recently the figure 3.862 has been published by Roth and Becker as the density of titanium oxide at 21° C.[36] The deviations so obtained (Table 7) were plotted against the titanium oxide concentration (Figure 5) in application of the theory of Dennison[35] that the deviation of a property from the mixture law indicates compound formation, and the point of maximum deviation the presence of a compound identical in composition with that of the solution regardless of the temperature at which the measurements may be made. For purposes of comparison the density deviation from the calculated for sulphuric acid solutions in a concentration range covering the concentrations of total acid present in the titanium sulphate solutions is given in Table 8, Figure 6. The density deviation curve for the titanium sulphate solutions, acidity factor 0.5 (Figure 5), does not show a maximum in the concentration range studied, and therefore the composition of any compounds which are present in these solutions is not indicated by the density deviation. The density deviation curve plotted for sulphuric acid shows a distinct maximum at 33 per cent sulphuric acid which would indicate according to J. L. R. Morgan[37] the presence of the compound $H_2SO_4 . 11H_2O$. This data is included in order to demonstrate that the deviation curves for the titanium sulphate solutions and for sulphuric acid solutions corresponding in concentration to the total acidity of the titanium solutions are not parallel. However one peculiarity of the density deviation curve of the titanium sulphate solutions may

Table 7.

Deviation of Observed Density from Calculated for Solutions with Acidity Factor 0.5.

Per Cent TiO_2 by wt.	Obs. Dens.	Calc. Dens.	Deviation
9.909	1.3774	1.5274	0.1500
9.504	1.3580	1.5057	0.1477
9.176	1.3409	1.4881	0.1472
8.767	1.3230	1.4663	0.1433
8.374	1.3045	1.4446	0.1401
7.965	1.2876	1.4233	0.1357
7.530	1.2689	1.4000	0.1311
7.112	1.2509	1.3777	0.1268
6.670	1.2321	1.3540	0.1219
6.204	1.2133	1.3288	0.1155
5.750	1.1950	1.2978	0.1028
5.230	1.1757	1.2781	0.1024
4.737	1.1568	1.2506	0.0938
4.224	1.1376	1.2231	0.0855
3.65	1.1181	1.1924	0.0743
3.04	1.0985	1.1597	0.0612
2.49	1.0788	1.1303	0.0515
1.88	1.0586	1.0977	0.0391
1.29	1.0385	1.0661	0.0276

be pointed out. Namely, at lower concentrations of titanium oxide the curve is a straight line up to a concentration of about 4.5 per cent titanium oxide, and above this concentration deviates sharply from the straight line. At this concentration, i. e., about 4.5 per cent titanium oxide, is also the point at which a minimum occurs in the precipitation-concentration curve (Figure 2). It seems probable that there is some change in the composition of the solution at this concentration evidenced by change in direction of the physical property curve as well as the precipitation curve. However, since the knowledge available concerning the composition and characteristics of titanium solutions is extremely limited, it is not possible to state at the present time the nature of the change which occurs.

Since the course of precipitation was the primary study of the investigation the question arose as to whether this irregular precipitation curve is characteristic of titanium sulphate solutions in gen-

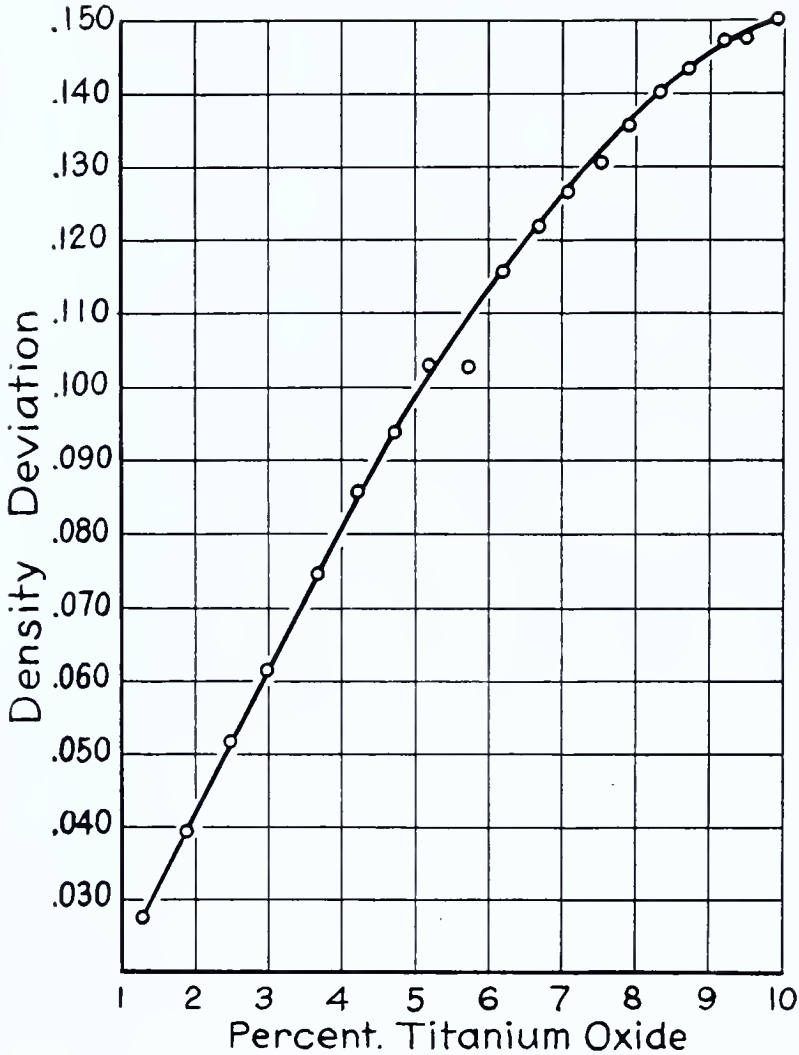


Figure 5. Deviation of observed density from the calculated; titanium sulphate solutions, acidity factor 0.52.

eral, or is peculiar to solutions with an acidity factor of 0.5. A series of investigations of solutions with acidity factors ranging from 0.1 to 3 and with a hydrolysis period ranging from one hour to twenty-four hours in the more acid solutions was planned. The stock solutions and dilutions were prepared and adjusted in the same manner as those of the preceding series. In those series

Table 8.

Deviation of Observed Density from Calculated for Sulphuric Acid Solutions.

Per cent H_2SO_4	Obs. Dens.	Calc. Dens.	Deviation
1	1.0038	1.0054	0.0016
2	1.0104	1.0137	0.0033
3	1.0169	1.0220	0.0051
4	1.0234	1.0302	0.0068
5	1.0300	1.0385	0.0085
6	1.0367	1.0468	0.0101
7	1.0434	1.0551	0.0117
8	1.0502	1.0634	0.0132
9	1.0571	1.0717	0.0146
10	1.0640	1.0799	0.0159
11	1.0710	1.0882	0.0172
12	1.0780	1.0965	0.0185
13	1.0850	1.1046	0.0196
14	1.0922	1.1132	0.0210
15	1.0994	1.1212	0.0218
16	1.1017	1.1296	0.0229
17	1.1141	1.1379	0.0238
18	1.1215	1.1462	0.0247
19	1.1290	1.1545	0.0255
20	1.1365	1.1628	0.0263
21	1.1441	1.1711	0.0270
22	1.1517	1.1793	0.0276
23	1.1594	1.1876	0.0282
24	1.1672	1.1959	0.0287
25	1.1750	1.2042	0.0292
26	1.1829	1.2125	0.0296
27	1.1909	1.2207	0.0298
28	1.1989	1.2290	0.0301
29	1.2069	1.2373	0.0304
30	1.2150		0.0306

when the acidity factor was greater than 1, longer hydrolysis periods were used, and the precipitation was carried out in air-tight sealed glass jars in an oven at 100° C. For the series with an acidity factor of 1 or less, the procedure was exactly the same as that previously described for the hydrolysis of the solutions with an acidity factor of 0.5.

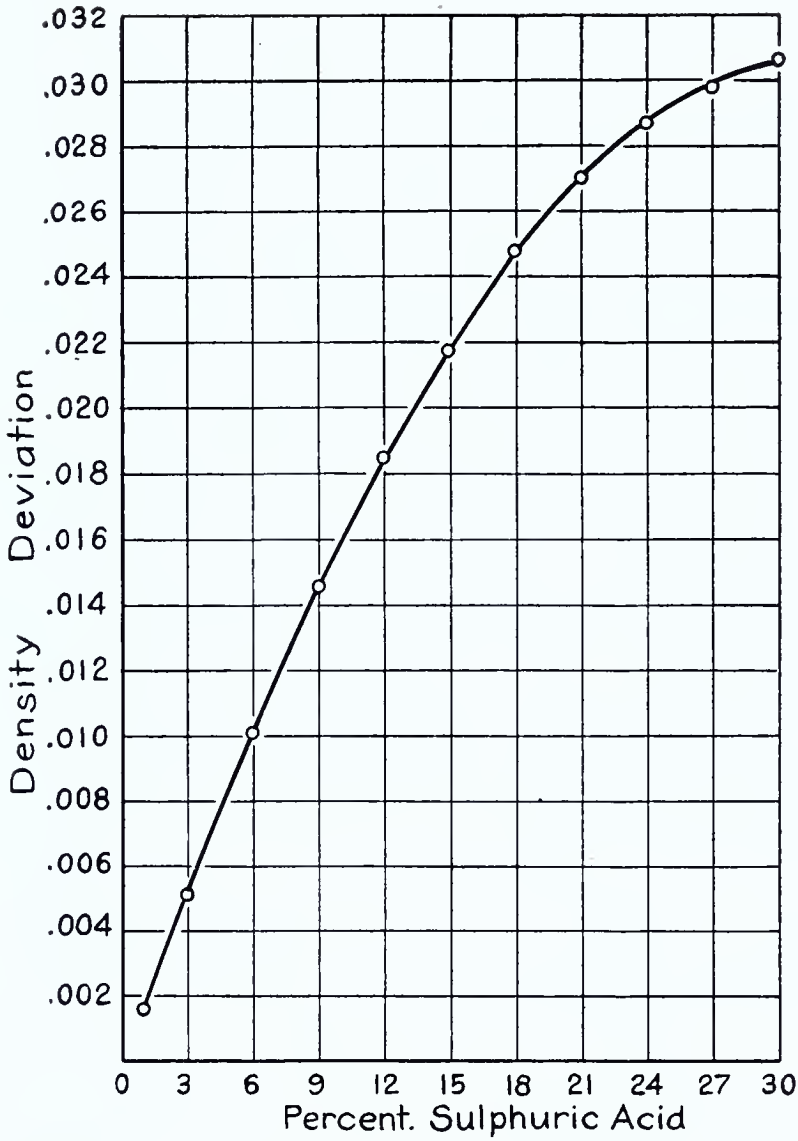


Figure 6. Deviation of the observed density from the calculated; sulphuric acid solutions.

Titanium Sulphate Solutions, Acidity Factor 0.1.

The stock solution used in this series gave the following analysis:

	per cent by weight	grams per liter
titanium oxide	10.01%	130.4
total sulphuric acid	25.52%	329.2
equivalent acid	24.50%	
excess acid	1.02%	
acidity factor	0.10	

Ten dilutions were made with distilled water keeping the acidity factor constant at 0.1 and varying the titanium oxide concentration from approximately one per cent to ten per cent by weight. Analysis of these solutions is given in Table 9.

Table 9.

Series II. Titanium sulphate solutions, acidity factor 0.1; concentrations of titanium oxide.

No.	Per cent by weight	Grams per 100 cc.
200	10.01	13.038
201	9.297	11.681
202	8.470	10.550
203	7.378	8.968
204	6.604	7.838
205	5.610	6.481
206	4.540	5.203
207	3.580	3.919
208	2.497	2.652
209	1.287	1.325

These solutions were precipitated by boiling under a reflux condenser as were those of Series I. Samples were withdrawn at the end of hourly periods of boiling with a total boiling time of eight hours. The results of the hydrolysis of Series II are summarized in Table 10 and Figures 7 and 8.

Figures 7 and 8 are plotted from the data in Table 10. In Figure 7 in which the per cent precipitated is plotted against the time during which hydrolysis has proceeded, for this series, as in Series I, only typical curves are plotted.

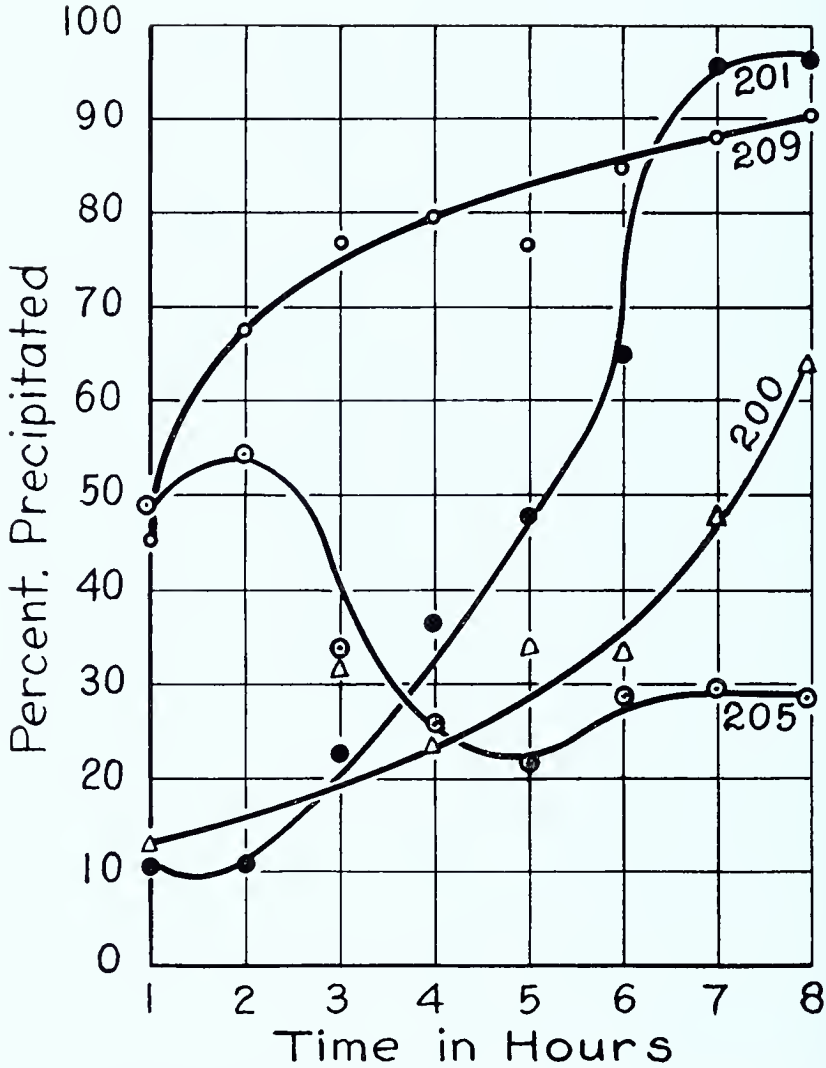
With this series of solutions, as with Series I, the course of precipitation over a given period of time varied with different concentrations of titanium oxide. The differences in concentration between the dilutions were small enough so that two or more of the solutions used always fell within each concentration range that had a specific effect on the course of precipitation. In plotting the data a typical curve in each range was selected as was done in Series I. In Figure 8 the per cent of titanium oxide precipitated at the end of eight hours of boiling was plotted against the titanium oxide concentration. The concentrations of titanium oxide plotted as showing the typical precipitation with time were also those which fell at maximum or minimum points in the precipitation-concentration curve, as well as the highest and lowest concentrations used.

Table 10.

Precipitation of Titanium Sulphate Solutions, Acidity Factor 0.1.

Soln. No.	Original concentration Per cent by vol.	Per cent TiO_2 by volume 1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.	8 hrs.
200	13.04	11.40		9.95	9.04	8.62	8.68	6.81	4.64
201	11.681	10.49	10.44	9.10	7.44	6.09	4.13	0.512	0.370
202	10.550	9.29	9.66	6.39	3.40	1.74	1.47	0.723	0.705
203	8.968	8.26	5.55	3.74	3.29	2.51	2.47	2.27	2.48
204	7.838	7.05	5.03	2.12	2.53	4.87	3.61	3.33	2.83
205	6.481	3.32	2.96	4.28	4.80	5.06	4.63	4.57	4.61
206	5.203	2.92	4.04	3.79	3.75	3.17	3.01	2.86	2.63
207	3.919	1.31	3.10	1.96	1.81	1.64	1.58	1.16	1.03
208	2.652	1.34	1.12	1.01	0.904	0.850	0.868	0.808	0.644
209	1.325	0.723	0.428	0.314	0.271	0.314	0.205	0.163	0.131

Soln. No.	Original concentration Per cent by wt.	Per cent precipitated 1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.	8 hrs.
200	10.01	12.60		31.35	22.97	33.87	33.41	47.74	64.35
201	9.297	10.20	10.60	22.06	36.31	47.87	64.64	95.61	96.83
202	8.470	11.99	8.45	39.42	67.72	83.54	86.00	93.14	93.32
203	7.378	7.90	38.15	58.32	63.29	72.15	73.61	74.65	72.32
204	6.604	10.00	35.85	72.92	67.73	37.89	53.96	57.50	63.84
205	5.610	48.84	54.36	33.96	25.91	21.86	28.60	29.53	28.84
206	4.540	43.92	22.37	27.23	29.90	39.15	42.07	44.96	49.41
207	3.580	66.55	20.79	50.01	53.74	58.15	59.73	70.50	73.82
208	2.497	49.66	57.76	61.80	65.91	68.70	67.27	69.53	75.72
209	1.287	45.43	67.69	76.37	79.54	76.30	84.52	87.70	90.11



200—10.01% titanium oxide 205— 5.61% titanium oxide
201— 9.30% " " 209— 1.29% " "

Figure 7. Influence of length of hydrolysis period on the per cent precipitated; titanium sulphate solutions, acidity factor 0.10.

In the most dilute solution studied, with an original titanium oxide concentration of 1.29 per cent by weight (curve 209 of Figure 7) slightly more than half the total precipitation during eight hours took place in the first hour, after which the rate of precipitation decreased. This closely resembles the course of precipitation for the most dilute solution of Series I, i. e., 1.32 per cent titanium oxide, acidity factor 0.5 (curve 109, Figure 1).

Curve 201, Figure 7, represents the course of precipitation of the sulphate solutions of 7.4 to 9.3 per cent titanium oxide, and is

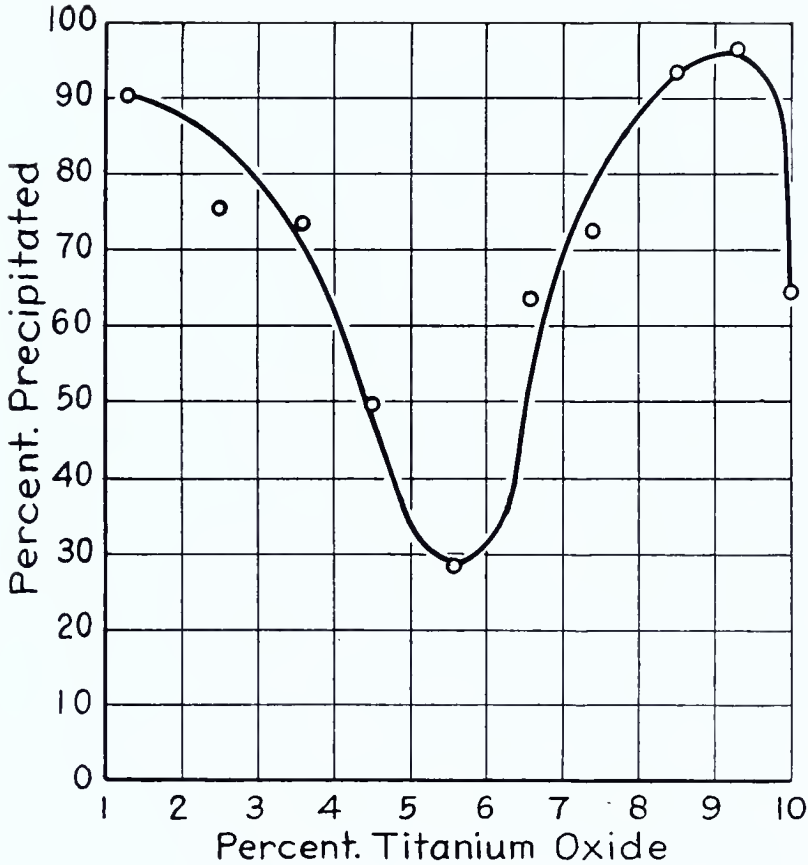


Figure 8. Influence of the titanium oxide concentration on the per cent precipitated in eight hours at the boiling point; titanium sulphate solutions, acidity factor 0.10.

plotted for the 9.3 per cent concentration. There was apparently at first a "lag" or induction period up to the third hour of boiling during which nuclei or centers of precipitation were probably set up, the per cent precipitated rising to only 20 per cent. During the next four hours the precipitation was the most rapid, the per cent precipitated rising from 20 to 95 per cent. Finally during the last hour observed the precipitation again proceeded rather slowly, only 2 per cent more of the titanium oxide precipitating to make the total amount precipitated 97 per cent of the original titanium oxide content. This mode of precipitation parallels closely that shown in curve 103, Figure 1. As in the previous series, it is in this concentration for which the precipitation has been plotted,

i. e., 9.3 per cent titanium oxide, that maximum precipitation in the eight hour period occurred.

The precipitation of the 5.6 per cent titanium oxide solution (curve 205, Figure 7), and which is representative of the sulphate solutions of from 3.6 to 6.6 per cent titanium oxide concentration, is peculiar in that after the second hour of boiling the hydrated titanium oxide which has been precipitated apparently redissolved until about the sixth hour after which the per cent precipitated remained very nearly constant. This solution is also peculiar in that of the whole series of titanium sulphate solutions of acidity factor 0.1, a minimum in the precipitation-concentration curve (Figure 8) occurs in this solution with a concentration of 5.6 per cent titanium oxide. The same observation was made in the previous series, in which a titanium sulphate solution of acidity factor 0.5 and 4.6 per cent titanium oxide concentration occurred at a minimum in the precipitation-concentration curve, and also gave the same type of precipitation-time curve.

Curve 200 of Figure 7 shows the amount precipitated with time for the most concentrated solution of this series, i. e., 10 per cent titanium oxide.

The per cent precipitated at the end of eight hours did not have any direct relationship to the titanium oxide concentration of the original solution (Figure 8). With increasing titanium oxide concentration above 1.3 per cent, there was a decrease in the per cent precipitated until a concentration, in the original solution, of 5.6 per cent titanium oxide was reached. Beyond this point the per cent precipitated rapidly rose with increased concentration up to 9.3 per cent titanium oxide at which concentration optimum precipitation for the concentration and time range studied occurred. It is only at this concentration that complete precipitation from the industrial point of view, i. e., with recovery of more than 90 per cent of the titanium oxide values of the solutions, took place. At higher concentrations the amount precipitated again decreased. For time periods of less than eight hours similar curves are obtained, but here, as in Series I, the marked minimum and maximum are not as sharply defined. The concentration of the solution in which maximum precipitation occurred varied with the length of the hydrolysis period. The longer the period over which hydrolysis takes place, the higher is the concentration of the solu-

tion in which maximum precipitation occurs. This is illustrated in Table 11, using data selected from Table 10. It may be seen from the table that the shift of the optimum precipitation concentration toward more concentrated solutions markedly decreases after the fourth hour indicating that a longer heating period would not give maximum precipitation in still higher concentrations of titanium sulphate solutions of this acid content.

Table 11.

Optimum precipitation occurred in:

1 hr.	in the	soln.	of	3.5%	TiO_2	by	wt.
2 hrs.	"	"	"	"	5.6%	"	"	"
3 hrs.	"	"	"	"	6.7%	"	"	"
4 hrs.	"	"	"	"	6.7-8.5%	"	"	"
5 hrs.	"	"	"	"	8.5%	"	"	"
6 hrs.	"	"	"	"	8.5%	"	"	"
7 hrs.	"	"	"	"	9.3%	"	"	"
8 hrs.	"	"	"	"	9.3%	"	"	"

Comparison of the figures and the data in the tables summarizing the course of precipitation of titanium sulphate solutions of acidity factors of 0.1 and 0.5 shows that the course of precipitation is not altered by this change in acidity factor. However, maximum precipitation occurs in solutions containing a higher concentration of titanium oxide when the acidity factor is lower, i. e., with an acidity factor of 0.1, a maximum precipitation of 97 per cent at the end of eight hours occurred in a solution containing 9.3 per cent titanium oxide, whereas with an acidity factor of 0.5, maximum precipitation, again 97 per cent at the end of eight hours, occurred in a solution containing originally 7.5 per cent titanium oxide. Similarly, the minimum in the precipitation-concentration curve occurs at a higher concentration of titanium oxide when the acidity factor is 0.1 than when the acidity factor is 0.5; the solution containing 5.6 per cent titanium oxide gave the minimum precipitation in eight hours in a series with an acidity factor of 0.1 whereas a solution containing 4.6 per cent titanium oxide gave minimum precipitation in eight hours when the acidity factor was 0.5. Consequently the precipitation-concentration curves of the two series for any given time period are similar in shape, but show maximum and minimum points at different concentrations of titanium oxide.

If the curves showing the course of precipitation with time for the two series are compared, it will be noted that the curves representing the same concentration of titanium oxide are not similar in shape, but that those which represent concentrations of titanium which fall at corresponding positions in the precipitation-concentration curve are similar in shape. For example, when the per cent precipitated in the solution originally containing 5.6 per cent titanium oxide with an acidity factor of 0.1 is plotted against time the curve does not resemble that for a solution containing 5.6 per cent titanium oxide with an acidity factor of 0.5 but is very similar to that for the solution containing 4.6 per cent titanium oxide with an acidity factor of 0.5; the 5.6 per cent titanium oxide solution with acidity factor of 0.1 and the 4.6 per cent titanium oxide solution with acidity factor of 0.5 both fall at the minimum point in their respective precipitation-concentration curves.

The two series of titanium sulphate solutions discussed above, one of acidity factor 0.5 and the other of acidity factor 0.1, showed marked similarity in hydrolytic behavior, with differences in degree but not in type. It was thought if a similar series of titanium sulphate solutions of intermediate acidity, for example with an acidity factor of 0.2, were hydrolyzed similar precipitation curves should be obtained; and the differences observed should be intermediate between those of the first two series, for example the titanium oxide concentration at which maximum precipitation occurs within eight hours of boiling should be between 7.5 and 9.3 per cent and nearer the higher concentration. Accordingly, to determine whether this would actually prove to be true a series (Series III) of titanium sulphate solutions of acidity factor 0.2 were prepared and hydrolyzed as before.

Titanium Sulphate Solutions, Acidity Factor 0.2.

A solution of pure titanium sulphate in dilute sulphuric acid was prepared as has been previously described. This solution analyzed:

	per cent by weight	grams per liter
titanium oxide	10.19	134.9
total sulphuric acid	26.89	356.1
equivalent acid	24.92	330.5
excess acid	1.97	25.6
acidity factor	0.19	

Ten dilutions of this solution were prepared containing titanium oxide from about 1 to 10 per cent by weight, the acidity factor remained constant. A sample of each dilution was retained for analysis and the bulk of the solutions immediately hydrolyzed by boiling under a reflux condenser. The analysis of these solutions is given in Table 12. As in the previous cases samples were withdrawn at the end of hourly boiling periods, with a total hydrolysis period of eight hours. These withdrawn samples were decanted, or filtered, and analyzed for titanium oxide content by reduction and titration against standard ferric alum solution. The per cent precipitated was then calculated from these results. The results obtained are summarized in Table 13 and Figures 9 and 10. In plotting the data showing the amount precipitated, or rather the per cent of the total titanium oxide originally present in the solutions precipitated, a typical curve representing the form of several such curves was selected as previously. Thus curve 300 (Figure 9) was plotted from the data on the precipitation of the solution of 10.2 per cent titanium oxide concentration, and a curve plotted for solution 301 (9.5 per cent titanium oxide) would show the same general shape, roughly paralleling the curve drawn. Likewise curve 302 plotted for the 9.1 per cent titanium oxide solution is similar in form to that which might be drawn for the 8.0 per cent solution. Again, curve 306 (4.6 per cent titanium oxide) has the characteristic shape of those representing the precipitation of the 6.0 and 6.8 per cent solutions. And finally, curve 309 (1.4 per cent titanium oxide) is similar in shape to those given by the 2.6 and 3.7 per cent titanium oxide solutions.

Table 12.

Series III. Titanium sulphate solutions, acidity factor 0.19; concentrations of titanium oxide.

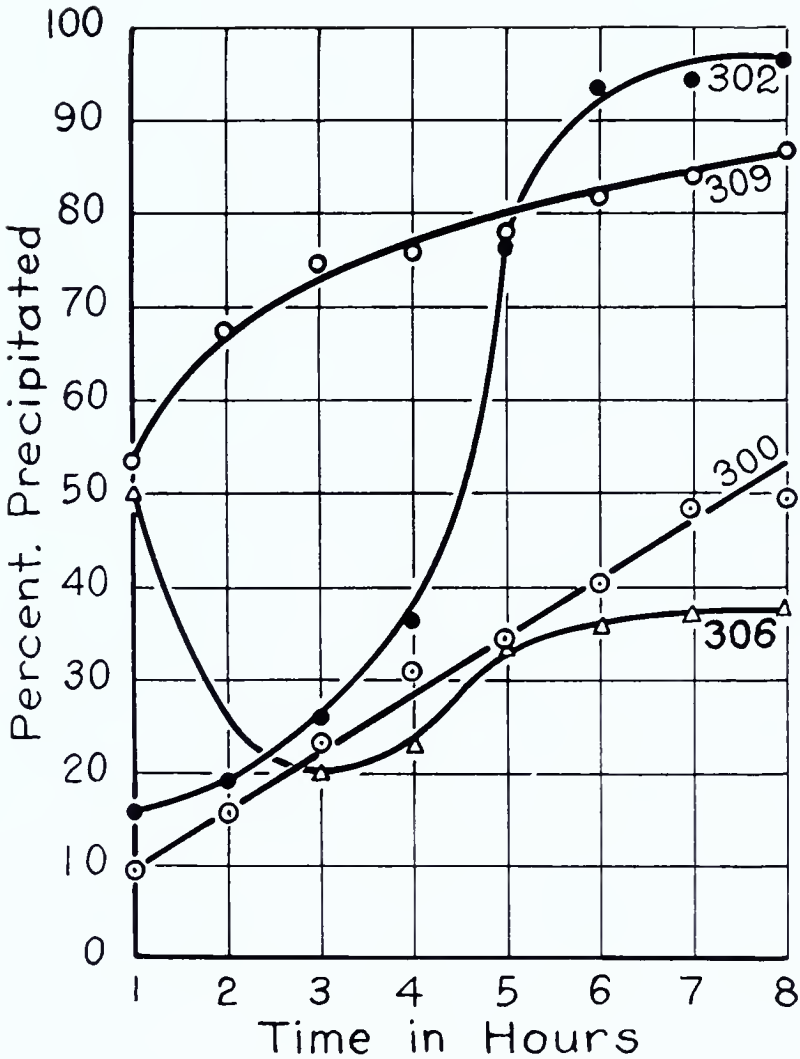
No.	Per cent by weight	Grams per 100 cc.
300	10.19	13.49
301	9.545	12.193
302	9.055	11.470
303	8.000	9.870
304	6.796	8.169
305	6.017	7.039
306	4.615	5.342
307	3.690	4.070
308	2.564	2.743
309	1.365	1.414

Table 13.

Precipitation of Titanium Sulphate Solutions, Acidity Factor 0.19.

Soln.	Original concentration	Per cent TiO_2 by volume							
No.	Per cent by vol.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.	8 hrs.
300	13.490	12.20	11.13	10.37	9.32	8.86	8.08	6.96	6.84
301	12.193	10.85	10.15	9.44	8.44	8.02	7.60	4.16	1.21
302	11.470	9.65	9.31	8.49	7.27	2.71	0.63	0.68	0.40
303	9.870	8.88	8.20	7.51	4.85	1.69	1.71	2.20	0.94
304	8.169	7.54	6.86	7.24	5.61	6.39	3.01	5.19	7.63
305	7.039	5.85	4.76	4.60	4.73	4.74	4.70	4.60	4.16
306	5.342	2.68	4.32	4.30	4.12	3.54	3.44	3.38	
307	4.070	2.87	2.40	2.55	1.93	1.32	1.63	1.34	1.10
308	2.743	1.46	1.24	1.05	0.87	0.87	0.79	0.70	0.63
309	1.414	0.663	0.464	0.362	0.34	0.31	0.26	0.23	0.19

Soln.	Original concentration	Per cent precipitated							
No.	Per cent by wt.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.	8 hrs.
300	10.19	9.54	15.32	23.05	31.01	34.31	40.11	48.38	49.27
301	9.545	11.00	16.79	22.62	30.86	34.24	37.70	65.88	90.11
302	9.055	15.91	18.80	25.98	36.66	76.34	93.37	94.09	96.53
303	8.00	10.03	16.92	23.91	64.07	82.88	82.67	77.71	90.48
304	6.796	7.75	16.10	11.36	31.36	21.76	63.11	36.53	6.64
305	6.017	11.92	32.33	34.57	32.19	32.67	33.14	36.11	40.90
306	4.615	49.78	19.15	19.76	22.96	33.69	35.68	36.80	
307	3.690	29.43	40.95	37.42	52.60	67.47	59.88	67.13	73.05
308	2.564	46.70	66.71	61.75	68.32	68.51	72.98	74.52	77.14
309	1.365	53.11	67.18	74.39	75.81	77.79	81.47	84.02	86.35



300—10.2% titanium oxide
302— 9.1% " "
306— 4.6% titanium oxide
309— 1.4% " "

Figure 9. Influence of length of hydrolysis period on the per cent precipitated; titanium sulphate solutions, acidity factor 0.2.

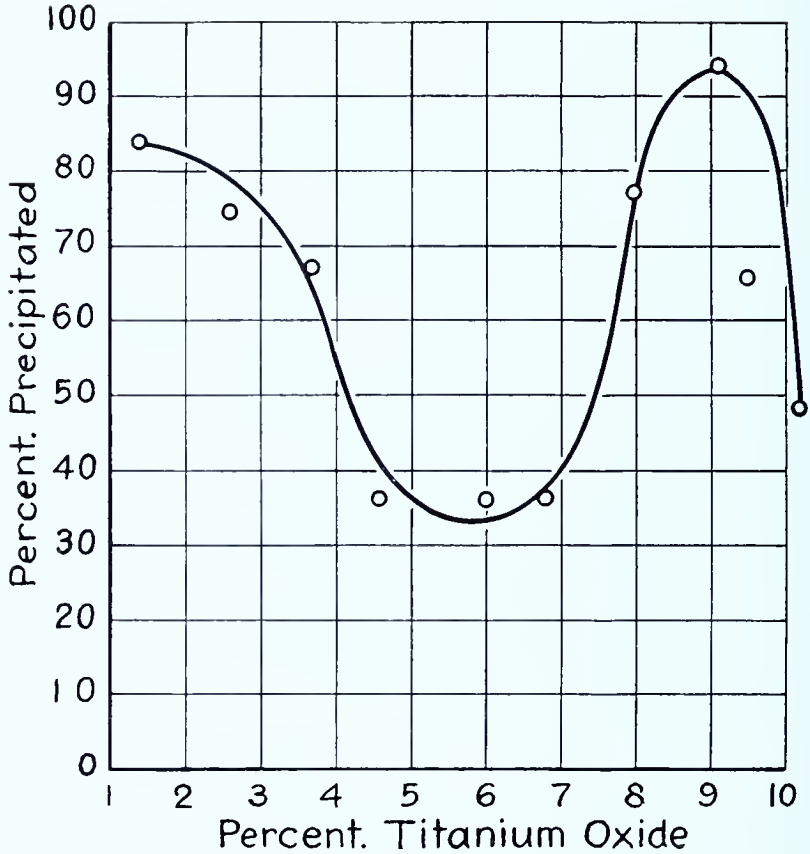


Figure 10. Influence of the titanium oxide concentration on the per cent precipitated in seven hours at the boiling point; titanium sulphate solutions, acidity factor 0.2.

From curve 300 it is seen that precipitation in the most concentrated solution used proceeded at an almost uniform rate during the eight hours of hydrolysis at the boiling point of the solution, and in this respect closely resembled the previously described solutions of similar concentration but acidity factors of 0.1 and 0.5. The precipitation rate was comparatively low, less than 50 per cent of the titanium oxide being precipitated in eight hours. In the slightly more dilute solution, 9.5 per cent titanium oxide, the rate of precipitation was greater, almost 90 per cent of the titanium oxide originally present precipitated during the eight hours of boiling.

The three most dilute solutions precipitated in a manner similar to the concentrated solutions just described. Curve 309 shows

that the rate of precipitation after the first hour was very nearly uniform during the next seven hours, as was the rate of precipitation for the most concentrated solutions discussed immediately above. In this most dilute solution, 1.4 per cent titanium oxide, the greatest part of the precipitation, 53 per cent precipitated, took place in the first hour; during the remaining seven hours the per cent precipitated increased but 33 per cent to a total of 86 per cent precipitated in eight hours.

In the precipitation of the 4.6 per cent titanium oxide solution (curve 306, Figure 9), which is in general similar to that of the sulphate solutions of from 4.6 to 6.8 per cent titanium oxide concentration, it is seen that after the second hour of boiling a considerable portion of the metatitanic acid which was precipitated redissolved, some 50 per cent of the titanium oxide originally present having precipitated in the first hour and but 19 per cent remaining out of solution at the end of two hours. After this second hour of re-solution precipitation again proceeded rather slowly, at the end of seven hours 37 per cent of the titanium oxide having been precipitated. This solution is also in the region of the minimum in the precipitation concentration curve (Figure 10) for the sulphate solutions of acidity factor 0.2. This same phenomenon, namely, re-solution of the titanium oxide first precipitated, also occurred in the titanium sulphate solutions of acidity factors 0.1 and 0.5 in the solutions which were at the minima in their respective precipitation-concentration curves.

The per cent precipitated at the end of seven hours again does not have any direct relationship to the titanium oxide concentration of the original solution (Figure 10). The shape of the curve obtained by plotting the per cent precipitated at the end of this time period against the titanium oxide concentrations is the same as that of similar curves for the solutions of 0.1 and 0.5 acidity factor. With increasing titanium oxide concentration, from 1.4 to 4.6 per cent, there was a decrease in the per cent precipitated. From 4.6 to 6.8 per cent the amount precipitated in seven hours is very nearly the same. Beyond this last point the per cent precipitated rapidly rose with increased concentration up to 9.1 per cent titanium oxide at which concentration optimum precipitation, 94 per cent, for the concentration and time range studied occurred. At higher concentrations, 9.5 to 10.0 per cent, the amount precipitated again decreased. The concentration of the

solution in which maximum precipitation occurred varied with the length of the hydrolysis period as is indicated in Table 14. As in the previous series optimum precipitation occurred in solutions of increasing concentration during the first six hours of boiling. On longer boiling the greatest amount of precipitation continued to take place in the same solution, i. e., one originally containing 9.1 per cent titanium oxide. It seems probable that with further boiling maximum precipitation would still have continued to occur in this solution.

Table 14.

Optimum precipitation occurred in:

1 hr.	in	the	soln.	of	4.6%	TiO_2	by	wt.
2 hrs.	"	"	"	"	6.0%	"	"	"
3 hrs.	"	"	"	"	6.0%	"	"	"
4 hrs.	"	"	"	"	8.0%	"	"	"
5 hrs.	"	"	"	"	8.0%	"	"	"
6 hrs.	"	"	"	"	9.1%	"	"	"
7 hrs.	"	"	"	"	9.1%	"	"	"
8 hrs.	"	"	"	"	9.1%	"	"	"

Comparison of the figures and data in the tables summarizing the course of precipitation of these titanium sulphate solutions of acidity factor 0.2 and those for the solutions of acidity factors 0.1 an 0.5 previously described shows that the course of precipitation was not altered by this change in acidity. As was expected, the specific effects of the acidity were in these solutions intermediate between those of the other series. Thus optimum precipitation occurred in a solution with an original concentration of 9.1 per cent titanium oxide, which is between 9.3 per cent which gave maximum precipitation when the acidity factor was 0.1 and 7.5 per cent titanium oxide which gave the maximum precipitation when the acidity factor was 0.5. As has been stated above, the course of precipitation was not altered by the change in acidity. This statement must be modified to some extent in that precipitation-time curves of the same general shape were obtained, not with titanium sulphate solutions of the same concentration, but at the titanium concentrations which fell at corresponding portions of the precipitation-concentration curves for the solutions of the three acidities used.

The acidity factors 0.1, 0.2 and 0.5, of the solutions thus far studied did not cover a very wide range of acidity. This might account for the similarity in the course of precipitation in these series of solutions. In order to determine whether or not a higher acidity might make a marked difference in the precipitation curve and also to include more solutions of practical interest several series of titanium sulphate solutions of higher acidities were investigated. A series (Series IV) of solutions with acidity factor of 1.0, twice that of the most acid solutions previously studied and ten times that of the least acid was prepared, and the hydrolysis carried out as before.

Titanium Sulphate Solutions, Acidity Factor 1.0.

A solution of titanium sulphate in dilute sulphuric acid was prepared from crystallized titanyl sulphate as has been already described. This solution analyzed:

	per cent by weight	grams per liter
titanium oxide	9.77	135.56
total sulphuric acid	33.90	470.25
equivalent acid	23.91	332.12
excess acid	9.99	138.13
acidity factor	1.02	

Ten dilutions of this solution were prepared containing titanium oxide from about 1 to 10 per cent by weight with the acidity factor constant. As in the previous series a sample of each dilution was retained for analysis and the bulk of the solutions immediately hydrolyzed by boiling under a reflux condenser. The analysis of these solutions is given in Table 15. As in the previous series samples were withdrawn at the end of hourly boiling periods, with a total hydrolysis period of eight hours. These withdrawn samples were decanted, or filtered, and analyzed for titanium oxide. The results of the analyses and the per cent precipitated calculated therefrom are given in Table 16. Some of the data from Table 16 is graphically presented in Figures 11 and 12.

Table 15.

Series IV. Titanium sulphate solutions, acidity factor 1.02; concentrations of titanium oxide.

No.	Per cent by weight	Grams per 100 cc.
400	9.77	13.56
401	8.88	11.81
402	8.196	10.76
403	7.270	9.265
404	6.432	7.959
405	5.552	6.666
406	4.501	5.232
407	3.520	3.955
408	2.485	2.686
409	1.301	1.356

In Figure 11 is plotted the per cent precipitated against the time of hydrolysis for four selected titanium sulphate solutions. The per cent precipitated at the end of the hourly boiling periods for the 9.8 per cent titanium oxide solution, the most concentrated of this series, is plotted as curve 400. It may be seen that the rate of precipitation was fairly constant over the eight hour period, very nearly a straight line being obtained, and was quite low, but little more than 10 per cent of the titanium oxide present having been precipitated. The same was true for the solutions of 8.2 and 8.9 per cent titanium oxide except that the precipitation rate was somewhat greater, 33 and 16 per cent respectively, of the titanium oxide having precipitated in eight hours.

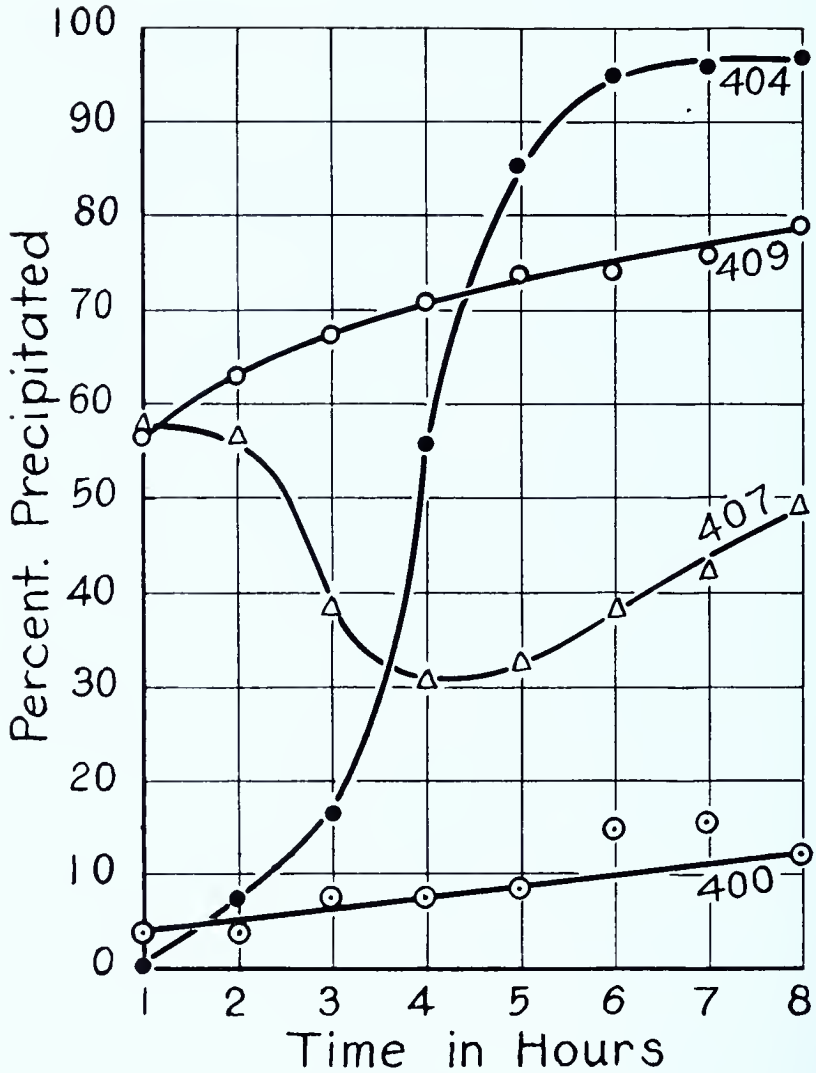
The precipitations of solutions of 5.6 to 7.3 per cent titanium oxide are represented by curve 404 which has been plotted from the data on the 6.4 per cent solution. It was in this solution that maximum precipitation for the series occurred, namely 97 per cent precipitated in eight hours. The curve showing the amount precipitated with time is of the same general shape as those for the solutions of other acidity factors in which the maximum precipitation for the series occurred. During the first three hours the rate of hydrolysis, as measured by the formation of an insoluble hydrated titanium oxide, was comparatively low and of the same

Table 16.

Precipitation of Titanium Sulphate Solution, Acidity Factor 1.02.

Soln. No.	Original concentration Per cent by vol.	Per cent TiO_2 by volume 1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.	8 hrs.
400	13.56	13.06	13.06	12.54	12.54	12.43	11.54	11.49	11.94
401	11.81	11.44	11.54	10.99	10.40	10.10	10.05	10.30	9.95
402	10.76	10.35	9.55	9.40	9.00	8.78	6.96	7.59	7.24
403	9.265	8.84	8.51	8.08	7.71	6.29	4.15	2.20	0.770
404	7.959	7.96	7.36	6.64	4.30	1.14	0.398	0.316	0.246
405	6.666	5.72	5.67	0.358	0.268	0.734	0.789	0.800	0.446
406	5.232	4.69	2.99	0.821	1.62	2.02	2.05	2.12	1.19
407	3.955	1.67	1.71	2.43	2.74	2.66	2.43	2.29	2.00
408	2.686	1.69	1.37	1.22	1.08	0.930	0.756	0.761	0.567
409	1.356	0.587	0.52	0.443	0.398	0.363	0.353	0.328	0.291

Soln. No.	Original concentration Per cent by wt.	Per cent precipitated 1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.	8 hrs.
400	9.770	3.69	3.69	7.53	7.53	8.34	14.90	15.27	11.95
401	8.880	3.13	2.29	6.94	11.94	14.47	14.90	12.78	15.74
402	8.196	3.81	11.25	12.64	16.32	18.41	28.06	29.47	32.72
403	7.270	4.64	8.19	12.76	16.67	32.08	55.17	76.26	91.69
404	6.432	0.00	7.50	16.56	45.94	85.62	95.00	96.03	96.91
405	5.552	14.18	14.93	94.63	95.71	88.99	88.17	88.00	93.31
406	4.501	11.97	43.93	84.39	69.51	62.06	61.42	60.20	77.61
407	3.520	57.75	56.74	38.61	30.72	32.72	38.69	42.20	49.56
408	2.485	37.04	49.07	54.43	59.64	65.51	71.85	71.66	78.88
409	1.301	56.73	63.01	67.35	70.67	73.25	73.99	75.83	78.57



400—9.8% titanium oxide
404—6.4% " "
407—3.5% titanium oxide
409—1.3% " "

Figure 11. Influence of the length of hydrolysis period on the per cent precipitated; titanium sulphate solutions, acidity factor 1.0.

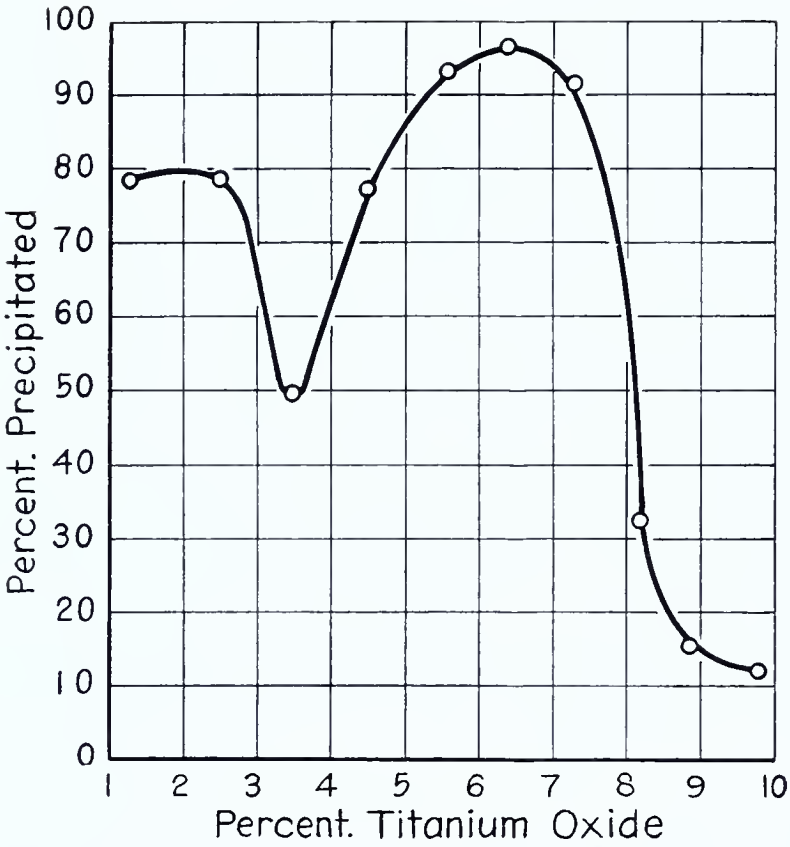


Figure 12. Influence of the titanium oxide concentration on the per cent precipitated in eight hours at the boiling point; titanium sulphate solutions, acidity factor 1.0.

order as of the most concentrated solutions used, but 16 per cent of the titanium oxide precipitating. Between the third and sixth hours the rate of precipitation was comparatively high, the per cent precipitated increasing from 16 to 95 per cent. Finally, during the last two hours very little precipitation occurred, the per cent precipitated rising but an additional 2 per cent to make the total precipitation during eight hours of boiling 97 per cent. Curves of similar shape, but with different and lower percentages of titanium oxide precipitated in the same time, would be obtained if the data for the solutions of 7.3 and 5.6 per cent were plotted.

Curve 407 represents the per cent precipitated with time in the 3.5 per cent titanium oxide sulphuric acid solution. It is in this solution that minimum precipitation in the given time period

occurred in the solutions between 1.2 and 6.4 per cent, and this curve has the same general shape as those of the other acidity factors which were at the minima in their respective precipitation-concentration curves. The greatest precipitation of hydrated titanium oxide took place during the first hour of boiling, 58 per cent of the titanium oxide present precipitating. During the next three hours re-solution of the metatitanic acid took place, the per cent precipitated decreasing to 31 per cent at the end of the fourth hour. During the remaining four hours of hydrolysis re-deposition of the oxide again took place, the per cent precipitated increasing at a relatively constant rate to 50 per cent.

The most dilute solutions of this acidity factor show a relatively constant rate of precipitation after the first hour. Curve 409 represents the per cent precipitated with time for the most dilute solution used, 1.3 per cent titanium oxide. During the first hour 57 per cent of the titanium oxide present was precipitated. During the remaining seven hours of the hydrolysis period the per cent precipitated increased fairly uniformily to 79 per cent. The same type of curve is given by the 2.5 per cent titanium oxide solution, the percentage precipitated being somewhat lower.

In Figure 12 the per cent precipitated in eight hours is plotted against the concentration of the titanium sulphate solutions. The curve so obtained is similar to the same curve for the other acidities studied, and as before the per cent precipitated in the given time period did not have any direct relationship to the concentration of the original solutions. Above 2.5 per cent titanium oxide, up to 3.5 per cent, with increasing concentration the per cent precipitated decreased. Between 3.5 and 6.4 per cent titanium oxide the per cent precipitated increased with increasing titanium oxide concentration to the latter concentration at which maximum precipitation for the series occurred. With further increase in concentration the per cent precipitated decreased quite rapidly. For time periods of less than eight hours similar curves would be obtained but the minima and maxima are not as sharply defined with a shorter hydrolysis period and gradually shift toward the more concentrated solutions with increased time. The shift in the maximum precipitation toward the more concentrated solutions with time is illustrated by Table 17.

Table 17.

Optimum precipitation occurred in:

1 hr.	in	the	soln.	of	3.5%	TiO_2	by	wt.
2 hrs.	"	"	"	"	3.5%	"	"	"
3 hrs.	"	"	"	"	4.5-5.5%	"	"	"
4 hrs.	"	"	"	"	5.5%	"	"	"
5 hrs.	"	"	"	"	5.5%	"	"	"
6 hrs.	"	"	"	"	6.4%	"	"	"
7 hrs.	"	"	"	"	6.4%	"	"	"
8 hrs.	"	"	"	"	6.4%	"	"	"

It had been found in Series I that an analysis of the hydrolytic products from titanium sulphate solutions of acidity factor 0.5 did not have any relationship to the concentration of the solution from which they had been precipitated. In order to confirm this, and also to determine whether the change in acidity factor had any definite effect on the composition of the precipitated metatitanic acid, some of the hydrolytic products of this series were also analyzed. At the end of eight hours of boiling the precipitated hydrolytic products were separated from solutions 400 (originally 9.8 per cent titanium oxide), 404 (originally 6.4 per cent titanium oxide), 407 (originally 3.5 per cent titanium oxide), and 409 (originally 1.3 per cent titanium oxide). These products selected for analysis were, as in the other series, from the most concentrated (400) and most dilute (409) solutions studied and also from the solutions which were at the minimum (407) and the maximum (404) on the precipitation-concentration curve for this series. As before, the precipitate in each case was collected on a Buchner funnel, washed free of titanium with dilute suphuric acid and free of acid with distilled water. They were air-dried for a week, powdered and allowed to dry for two more days. Moisture was determined as the loss in weight on drying forty-eight hours at 105° C. The sulphate content was estimated as described in the beginning of this report by fusing with sodium carbonate, digesting, filtering and precipitating the sulphate from the filtrate as barium sulphate which was separated, ignited and weighed. Combined water was determined by igniting the dried hydrolysis product and determining residual sulphate after ignition; the combined water then being the loss on ignition less the sulphuric anhydride

lost on ignition. Titanium oxide was estimated by solution in sulphuric acid, reduction and titration with standard ferric alum solution. The results of these analyses are tabulated in Table 18. In this group the statement of A. J. Rossi and L. E. Barton[20] that excessive dilution during hydrolysis yields products lower in sulphuric anhydride is found to be applicable. The sulphuric anhydride content dropped from 7.27 per cent in the precipitate from the 9.8 per cent titanium oxide solution to 3.08 per cent in the precipitate from the 1.3 per cent solution. No correlation exists between these analyses and those of products precipitated from the solutions of lower acidity (Series I); and there is no apparent affect by the acidity, within the limits of acidity factors 0.5 to 1.0, on the composition of the metatitanic acid formed. It must be recognized that analyses made in the way described probably do not represent the composition of the products as precipitated. Different products may very well respond quite differently to the washing and drying method used, which, of course would not be indicated in the analysis, i. e., with different products varying amounts of sulphate may be removed on prolonged washing, or more of the combined water may be lost on drying at 105°.

Table 18.

Analysis of Precipitation Products, Titanium Sulphate Solutions.

Acidity Factor 1.0.

Soln.	Orig soln. % TiO_2	Moisture %	TiO_2* %	SO_3* %	H_2O* %	Total* %
400	9.77	6.31	85.66	7.27	7.07	100.00
404	6.43	7.88	85.04	5.24	9.19	99.47
407	3.52	8.86	87.57	4.30	7.96	99.83
409	1.30	7.83	89.73	3.08	7.14	99.95

* On dry basis.

Although there is no apparent correlation between the composition of the hydrolytic products, as shown by these analyses, when the acidity factor is 1.0 and those precipitated from a solution of acidity factor 0.5, the course of precipitation of the solutions of different acidity factors show marked similarities.

In all the series when the per cent precipitated in a given time period, for example eight hours, was plotted against the titanium oxide concentrations of the original solutions, curves of the same general shape were obtained, i. e., they showed a decrease in the per cent precipitated with increased titanium concentration up to a certain point beyond which the per cent precipitated increased with increasing concentration, forming a minimum in the curve. This increase in precipitation continued to a concentration at which maximum precipitation for the series occurred. With further increase in concentration the percentage precipitation rapidly decreased, forming a maximum in the curve. Furthermore, while these maxima and minima occurred in solutions of different concentrations in the series of different acidity factors, the course of the precipitation of the solutions which fall at these points on the precipitation-concentration curve was quite similar, as is shown by plotting the per cent precipitated against the time of hydrolysis. The most dilute and most concentrated solutions used also showed quite similar hydrolytic behavior, as may be observed by comparison of their precipitation-time curves. The effect of acidity factor, between the limits of 0.1 to 1.0 is shown somewhat more clearly in Table 19. The table indicates the per cent precipitated in eight hours for the most dilute and most concentrated solutions used, for those solutions in which maximum precipitation occurred, and for those solutions which were at the minimum in the precipitation-concentration curve.

Considering the most dilute solution in each series, the horizontal column #1 in the table, it may be seen that the amount precipitated decreased with increase in acidity. It is also to be noted that in every series these dilute solutions all precipitated to the greatest extent during the first hour, after which the rate of precipitation was comparatively constant and low.

Increase in the acidity factor caused greater precipitation in the eight hour period, in those solutions which were at the minimum in the precipitation-concentration curve of each series. This increased precipitation with increased acidity factor is not peculiar if it is considered that the minimum in the precipitation-concentration curve occurs in more dilute solutions with the higher acidities. We know, from a consideration of the precipitation of the titanium solutions within each series that with increased dilution of the titanium solutions below that concentration at the minimum

Table 19.

Effect of Acidity Factor on the Per Cent Precipitated in Eight Hours at the Boiling Point of Titanium Sulphate Solutions.

Acidity Factor	0.1		0.2		0.5		1.0	
	% TiO_2	% Hyd.	% TiO_2	% Hyd.	% TiO_2	% Hyd.	% TiO_2	% Hyd.
1 Dilute	1.3	90.1	1.4	86.4	1.3	81.8	1.3	78.6
2 Minimum	5.6	28.8	4.6	36.8	4.6	44.4	3.5	49.6
3 Maximum	9.3	96.8	9.1	96.5	7.5	97.3	6.4	96.9
4 Concentrated	10.0	64.4	10.2	49.3	9.9	31.4	9.8	12.0

in the precipitation-concentration curve, the amount of precipitation was very much greater. The hydrolysis of all these solutions was characterized by considerable precipitation in the first hour followed by re-solution of the precipitate during the next few hours and but slight further hydrolysis or re-precipitation during the remainder of the boiling period.

Maximum precipitation occurred in progressively more dilute solutions as the acidity was increased as indicated in horizontal column #3 of the table. Thus maximum precipitation took place in a solution containing 9.3 per cent titanium oxide of acidity factor 0.1; whereas, in the series of solutions of acidity factor 1.0 maximum precipitation was found to have been in the solution of only 6.4 per cent titanium oxide. The per cent precipitated was very nearly the same in all cases. *It is evident from this that in the industrial precipitation of titanium oxide, in which it is desirable to obtain yields of 90-95 per cent, it is necessary to regulate the acidity factor as well as the titanium oxide concentration, and to select the proper acidity for the titanium concentration which can be most readily and economically obtained.* The precipitation of these solutions all proceeded in the same way. During the first few hours of boiling the rate of precipitation was quite slow; this was then followed by a period of rapid precipitation, and finally in the last few hours the rate rapidly decreased and there was but little further precipitation.

The course of precipitation of the most concentrated solutions used in the series resembled that of the most dilute solutions, except that the amount, or rather per cent, precipitated was very much less. As in the dilute solutions, the rate of precipitation over the eight hour boiling period was very nearly constant, and likewise with increased acidity the amount precipitated was very much less (see horizontal column #4 of the table).

Both the acidity and the titanium oxide concentration have been shown to be important factors in the precipitation of the titanium sulphate solutions thus far studied. It was desired to learn whether the effects of increased acidity noted above extended to solutions of still greater acidity. Therefore such solutions were prepared and hydrolyzed.

Since with increased acidity it had been found that maximum precipitation, in an eight hour period, occurred in solutions of

lower concentration of titanium oxide, it was thought advisable to hydrolyze for a longer period of time in order to determine whether maximum precipitation might occur in a solution of higher concentration. For convenience these precipitations were carried out in glass-topped preserving jars sealed with a rubber ring or gasket, which were placed in a Freas electric oven at 100°C.

Titanium Sulphate Solutions, Acidity Factor 2.0.

An acid titanium sulphate solution was prepared which had the composition:

	per cent by weight	grams per liter
titanium oxide	9.96	144.69
total sulphuric acid	44.82	652.08
equivalent acid	24.35	354.07
excess acid	20.47	298.01
acidity factor	2.06	

Ten dilutions of this solution were prepared for precipitation. The analyses of these dilutions are given in Table 20.

Table 20.

Series V. Titanium sulphate solutions, acidity factor 2.06; concentrations of titanium oxide.

No.	Per cent by weight	Grams per 100 cc.
500	9.96	14.47
501	9.33	13.01
502	8.49	11.71
503	7.46	10.10
504	6.67	8.70
505	5.87	7.31
506	4.76	5.79
507	3.96	4.41
508	2.66	2.92
509	1.39	1.46

These solutions were placed in glass-topped preserving jars, sealed by means of a rubber ring or gasket, and placed in a Freas electric oven at 100° C. At intervals of four, six, eight, twelve and twenty-four hours, one jar containing each dilution was removed from the oven, allowed to cool, and the decanted or

filtered solution analyzed for titanium oxide. The results obtained are summarized in Table 21.

Table 21.

Precipitation of Titanium Sulphate Solutions, Acidity Factor 2.06.

Soln.	Original concentration		Per cent precipitated				
No.	% by wt.	% by vol.	4 hrs.	6 hrs.	8 hrs.	12 hrs.	24 hrs.
600	9.96	14.47	1.6*	55.1*	11.1*	51.1*	80.0*
601	9.33	13.01	3.8*		10.1*	43.1*	48.0*
602	8.49	11.71	3.5*	3.2*		4.8**	6.6**
603	7.46	10.10	4.5*	4.8*	20.9**	23.3**	2.3**
604	6.67	8.70	6.4	10.1**		4.9	73.0**
605	5.87	7.31	5.2	4.2		5.6	6.3
606	4.76	5.79	5.0	50.7		10.3	5.0
607	3.96	4.41	8.5	88.0		69.3	43.3
608	2.66	2.92	50.0	43.3		44.0	53.9
609	1.39	1.46	29.9	72.4		62.6	52.2

* Precipitate completely soluble in water.
** Precipitate partially soluble in water.

Perhaps the most notable thing in this series is the fact that in the higher concentrations of titanium oxide crystallization of titanyl sulphate occurred alone or together with precipitation of metatitanic acid. In the solutions of between 6 and 9 per cent titanium oxide precipitation of the meta acid as well as crystallization took place as indicated by the fact that the precipitate formed was only partially soluble in water. In the two solutions of greater

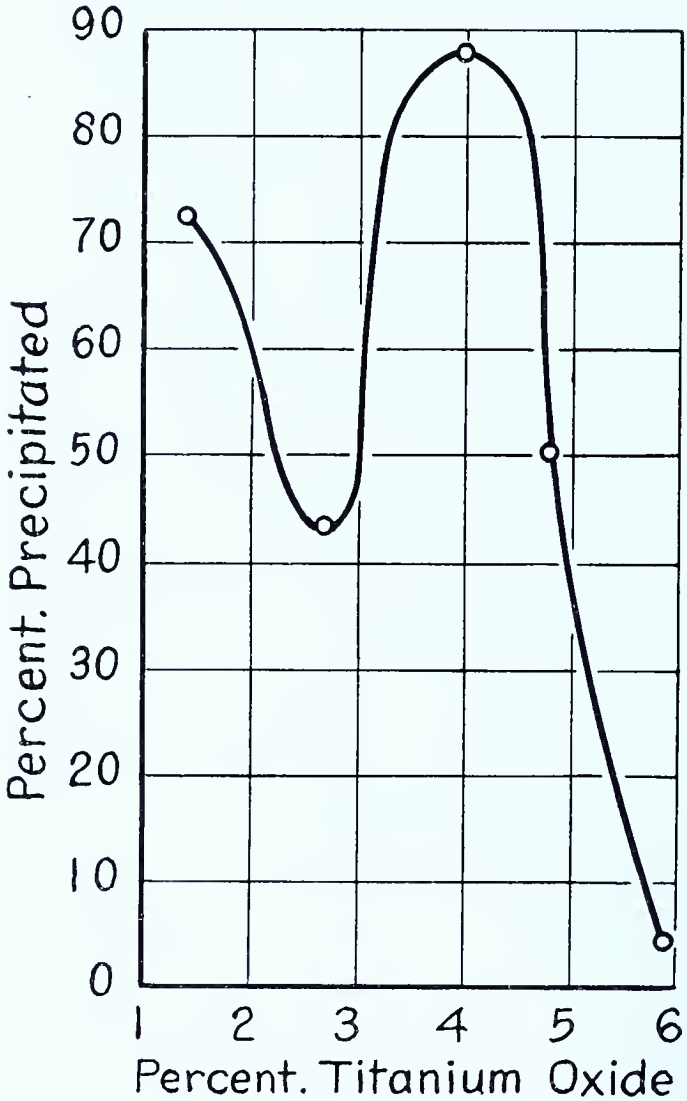


Figure 13. Influence of the titanium oxide concentration on the per cent precipitated in six hours at 100°C.; titanium sulphate solutions, acidity factor 2.06.

concentration than 9 per cent titanium oxide only crystallization of titanyl sulphate occurred inasmuch as the precipitate which formed was distinctly crystalline in character and completely soluble in water.

The results obtained for this series are not as regular as were the results for the precipitation of the solutions of lower acidity previously studied. This is probably because of the additional complication of crystallization of a water soluble titanyl sulphate in addition to the precipitation of relatively insoluble hydrated titanium oxides.

One point of interest is the fact that it was possible to crystallize titanyl sulphate with a reasonably high yield, e. g., 80 per cent in twenty-four hours at 100°C., from solutions of considerably lower concentrations of titanium oxide than those specified by J. Blumenfeld,[36] wherein the conditions for the crystallization of titanyl sulphate are stated to be: a temperature of 110-130°C., a titanium oxide concentration of 200 grams per liter, sulphuric acid content of 500 grams per liter, and a specific gravity of 1.45-1.615. The most concentrated solution used in the above series and found to give a reasonably good yield of crystalline titanyl sulphate was heated at 100°C. and contained but 145 grams per liter of titanium oxide, although the sulphuric acid concentration of 652 grams per liter was greater, and the specific gravity was about 1.46.

However, it should be noted that for those solutions of this series which were of lower titanium sulphate concentration than those in which crystallization occurred, the course of precipitation closely resembled that of the other series studied. Examination of the precipitation-concentration curve (Figure 13) shows the maximum and minimum points that seem to be characteristic of the course of precipitation of these solutions. In six hours at about 100°C., maximum precipitation occurred in a solution originally containing 3.96 per cent titanium oxide. Among the solutions of acidity factor 1.0 maximum precipitation occurred in the 6.4 per cent titanium oxide solution. This is in agreement with the previous finding that with increased acidity maximum precipitation occurs in more dilute, as respects titanium oxide concentration, solutions. When the hydrolysis period was extended to twelve hours the maximum precipitation again occurred in the

same concentration and not in a solution of higher titanium oxide content, but in the four-hour period maximum precipitation occurred in the solution which originally contained 2.7 per cent titanium oxide. This too is in agreement with the findings in previous series that the concentration of the solution which gives maximum precipitation increases with increased time of hydrolysis up to six hours, and then does not increase further with a longer precipitation period.

Titanium Sulphate Solutions, Acidity Factor 2.9.

A series of solutions of still greater acidity, acidity factor 2.9, was precipitated under similar conditions to those described just above. Titanium oxide concentrations greater than 6 per cent were not used because it had been found that crystallization of titanyl sulphate rather than precipitation of metatitanic acid took place in such solutions. The results obtained in this series are summarized in Table 22.

Table 22.

Series VI. Precipitation of Titanium Sulphate Solutions, Acidity Factor 2.9.

Soln. No.	Original concentration Per cent by vol.	Per cent precipitated 4 hrs.	8 hrs.
600	6.2	3.2	9.2
601	4.8	16.5	72.6
602	3.2	59.4	85.3
603	2.4	77.7	62.4
604	0.4	19.0	27.6

It will be noted that maximum precipitation at the end of eight hours occurred in a solution of only 3.2 per cent titanium oxide by volume, as compared to the previous series of acidity factor 2.0 in which maximum precipitation was in the solution of 4.4 per cent titanium oxide by volume. If the precipitation-time curve for this solution is plotted it shows the same characteristics as those of the solutions in the other series which gave maximum precipitation in eight hours; there is rapid precipitation between the fourth and eighth hours—from 59 to 85 per cent and then very little increase in the per cent precipitated over a longer period.

SUMMARY AND CONCLUSIONS.

The course of precipitation of pure titanium sulphate solutions ranging from one to ten per cent by weight of titanium oxide, with acidity factors varying from 0.1 to 2.9 and with a precipitation period from one to twenty-four hours has been studied. These concentrations and acidities cover the range commonly used in the industry.

In the first four series the course of precipitation at the boiling point of solutions of titanium sulphate of concentrations from 1 to 10 per cent titanium oxide with a constant acidity factor in each series, and over time intervals of one hour for eight hours was studied. The acidity factors used were 0.1, 0.2, 0.5 and 1.0. In such a series the rate of precipitation does not bear a direct relationship to the time or to the concentration of titanium sulphate.

With increasing concentration of titanium sulphate the precipitation decreases to a minimum then again rises until a maximum point is reached and then with still higher concentration the precipitation again shows a decrease. This is true regardless of the length of the hydrolysis period for those solutions and time periods studied. However, the concentration at which the maximum precipitation occurs increases with increase in the hydrolysis period up to six hours; if the hydrolysis period is longer than six hours, maximum precipitation occurs in the solution of the same concentration as that which showed the greatest precipitation in six hours.

The relationship of the course of precipitation to increased time depends upon the concentration of the titanium sulphate solution. With different acidities the precipitation-time curves for solutions of the same titanium oxide concentration are not similar, but those representing concentrations of titanium oxide which fall at corresponding positions in the precipitation-concentration curves are similar in shape.

In the last two series the precipitation of the solutions of higher acidity was carried out over longer time periods, and in an oven at 100°C. The acidity factors used were 2.0 and 2.9. Here again the course of precipitation shows no direct relation to time or concentration. In every series the precipitation-concentration curve shows the marked maximum and minimum point charac-

teristic of the course of precipitation of these solutions, and the concentration in which maximum precipitation occurs increases with increased length of the hydrolysis period up to a definite time and is then constant. In these series, however, titanyl sulphate crystallized from solutions containing more than 6 per cent titanium oxide. It is also true in these series that the form of the precipitation-time curve is dependent upon the concentration of the titanium sulphate solution.

For all of the series studied it may be observed that over a definite hydrolysis period, as the acidity factor is increased, the titanium oxide concentration of the titanium sulphate solutions in which maximum precipitation occurs is lower (Table 23). The minimum point in the precipitation-concentration curve also occurs in a solution of lower concentration of titanium oxide as the acidity is increased.

Table 23.

Influence of Acidity Factor on Precipitation.

Acidity factor	Hyd. time hrs.	Concentration which gave maximum precipitation Wt. %TiO_2	Vol. %TiO_2	Maximum % precipitated
0.1	8	9.3	11.7	97
0.2	8	9.1	11.5	97
0.5	8	7.5	9.4	97
1.0	8	6.4	8.0	97
2.0	6&12	4.0	4.4	88
2.9	8		3.2	85

It may also be noted in Table 23 that the maximum per cent precipitated decreased with increased acidity. It is also true that in the most dilute and the most concentrated solutions studied the per cent precipitated in a given time decreased with increased acidity.

Concentration of titanium oxide, length of hydrolysis and acidity factor are therefore all factors which affect the course of precipitation of the titanium sulphate solutions studied.

1. A method of preparing pure titanium sulphate solutions was devised. Titanium tetrachloride was hydrolyzed in the presence of titanous chloride and oxalic acid, the hydrated titanium

oxide precipitated was converted to the sulphate by means of hot concentrated sulphuric acid, this sulphate then dissolved in water and titanyl sulphate dihydrate crystallized by heating.

2. Precipitation is not a regular function of the concentration, and definite concentration ranges have a specific effect upon the course of precipitation when both the time period and acidity factor are constant.

3. In the most dilute solutions used, the rate of precipitation during the first hour is much higher than that of the most concentrated solutions used; after the first hour's precipitation the rate is about the same for the most concentrated and the most dilute solutions.

4. With increased length of hydrolysis time up to six hours, the concentration of the solution in which maximum precipitation occurs is greater; further increase in hydrolysis period gives maximum precipitation in the same concentration of titanium oxide with slight increase in the total per cent precipitated.

5. With increased acidity factor the titanium oxide concentration of the titanium sulphate solutions in which maximum precipitation occurs is lower.

6. The maximum per cent precipitated in the time periods studied decreases with increased acidity.

7. The concentration of titanium oxide has more influence on the rate of precipitation than the acidity factor. Thus in those solutions at the minimum of their respective precipitation-concentration curves the per cent precipitated increased in spite of increased acidity factor because these solutions occurring at the minima of the precipitation-concentration curves are more dilute as the acidity factor is raised.

8. In the most dilute and the most concentrated solutions the shape of the precipitation-time curves is the same for all acidities studied but the per cent precipitated in a given time decreases with increased acidity factor.

9. When the acidity factor is two or higher titanyl sulphate is crystallized alone or with metatitanic acid from solutions containing more than six per cent by weight of titanium oxide.

10. When the acidity factor is one or less than one, solutions of six to ten per cent by weight of titanium oxide may be 95 per cent precipitated by boiling for eight hours.

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